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INTERNATIONAL CHEMICAL SERIES

LOUIS P. HAMMETT, PH.D., *Consulting Editor*

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THEORETICAL
QUALITATIVE ANALYSIS

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LOUIS P. HAMMETT, PH.D., *Consulting Editor*

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THEORETICAL QUALITATIVE ANALYSIS

by J. H. REEDY
Associate Professor of Analytical Chemistry
University of Illinois

First Edition

FOURTH IMPRESSION

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PREFACE

As indicated by the title, this book proposes to furnish the student who is beginning analytical chemistry with the facts and theories upon which qualitative and quantitative analysis is based. This background of descriptive and physical chemistry is necessary if the student is really to understand what he is doing. Without it, analysis is certain to lapse into mechanical procedures, usually memorized but seldom understood.

This volume is intended to be a study book for the beginner, and not a reference book for the analyst. It does not propose to be exhaustive or even complete in its treatment. Critical reviewers will find many things missing and many others discussed in a superficial way. It has been the effort of the author to present the material in the simplest manner, so that the student will not be confused by fine distinctions and irrelevant statements. Citations to chemical literature have been omitted, for it has been found that elementary students make no use of them.

An explanation of the treatment of the theory of ionization seems in order. Both theories—the partial ionization theory of Arrhenius and the complete ionization theory of Debye and other modern physicists—are outlined. In the applications and problems, however, the approach has been mainly that of incomplete ionization. This seems desirable for two reasons: (1) the data for activities are limited, and (2) the mathematical treatment of incomplete ionization is much simpler. An attempt has been made to present both sides in an unbiased way, so that the student will not carry over into later courses an undue prejudice in favor of either theory.

Since most students will use the book largely in the study of assignments, the discussion of each topic has been made as complete as possible. This has involved repetition; but, on the whole, this may be desirable, for it gives drill on troublesome points. The problems and exercises are extensive and should be sufficient for several years' use without much repetition.

Free use has been made of the literature of analytical chemistry, especially the excellent texts of Treadwell-Hall and McAlpine-Soule. The author also acknowledges with appreciation the cooperation of the staff of analytical chemistry at the University of Illinois, particularly Drs. S. T. Gross and B. C. Marklein, who criticized the manuscript and assisted in reading the proof.

J. H. REEDY.

URBANA, ILLINOIS,
November, 1938.

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PART I
THEORETICAL

CHAPTER I

INTRODUCTION

Analytical chemistry deals with the methods used in determining the composition of various materials. When only the kinds of matter are sought, the process is called *qualitative analysis*; if the amounts of the various components are also to be ascertained, the process is *quantitative analysis*.

Quantitative Aspects of Qualitative Analysis.—There is no sharp distinction between qualitative and quantitative analysis. Every qualitative analysis should be quantitative to the extent that the analyst should distinguish between the principal and the minor components present in the material. Suppose that a chemist examined a white powder obtained at the family grocery and reported that it contained calcium, magnesium, sodium, chloride, iodide, and sulfate. Considerable doubt might be entertained, not only as to the name of the substance, but also as to what uses it might safely be put. But if he reported it to contain mainly sodium and chloride, along with traces of magnesium, calcium, iodide, and sulfate, we would instantly recognize the material as common salt, with its usual impurities of magnesium chloride, magnesium iodide, and calcium sulfate.

Again, the fundamental principles and reactions are the same in both qualitative and quantitative analysis. The most important difference is found in the technique of quantitative analysis, where an element must be separated in a weighable, or otherwise measurable, form. Many students delude themselves with the idea that there is no need for the reactions of qualitative analysis being quantitative. Many of the errors of the beginner can be traced to this notion.

Components.—To the analyst, component does not always mean element; very frequently it means radical. A knowledge of the radicals present in the material under examination is often of greater value than a knowledge of the elements. For example, an elemental analysis (formerly called *ultimate analysis*) shows a

certain substance to contain C, H, O, and N. Such a substance might be urea, albumen, Limburger cheese, or even nitroglycerin. On the other hand, if the material is tested for the ions or radicals present (*i.e.*, a *proximate analysis*), the substance is shown to contain nothing but NH_4^+ and CO_3^{--} . It is therefore seen to be ammonium carbonate, and no other possibility need be considered. Sometimes in the course of an analysis, the ions undergo changes, or even substitutions. To illustrate: Mn^{++} is tested for as MnO_4^- ; NO_3^- as NH_3 ; and Sn^{++} as Hg_2Cl_2 . It is therefore necessary for the analyst to reason back from his results to the radicals originally present.

Only in the case of metals and alloys may the composition of unknowns be reported as the ultimate components. To illustrate: a solution of salt does not contain Na and Cl, but Na^+ and Cl^- . It would be equally incorrect to report that a substance containing a permanganate contains Mn or Mn^{++} . There are cases, of course, where the analyst cannot be sure of the valence of certain of the component elements. But whenever it is possible, the report should show the ion or radical, and not the element.

HISTORICAL

Chemistry, in its broadest sense, is as old as civilization itself. Prehistoric man knew how to smelt some of the nobler metals, from which he made tools, weapons, etc.; he knew something about dyeing, pottery, embalming, and a few others of the industrial arts. In seeking for new materials for his work, he simply subjected a sample of the unknown substance to a small-scale industrial operation, and in this way the science of analysis developed.

Analytical chemistry is more fundamental to the chemical arts than most people realize. It is prerequisite to all the other branches—inorganic, organic, physical, and physiological. Before any work can be done, the composition of the materials must be known. To obtain this information, the substance is first subjected to a qualitative analysis. This is necessary to know what methods may be used in the next step, quantitative analysis. This is a point frequently overlooked by students in quantitative chemistry. How all chemical research depends, first, on qualitative analysis and, second, on quantitative analysis, is clearly brought out in the history of chemistry.

The Alchemists.—Throughout the Dark Ages, scientific thought was dominated by the teachings of the Greek philosophers. According to them, matter was a mixture of four elements: *viz.*, air, earth, water, and fire. Sometimes a fifth element, the “quintessence,” was included. The last was a philosophical concept, without any objective reality. Later, matter—more particularly, the metals—was thought to consist of mercury, sulfur, and salt, combined in various proportions. Therefore, since materials differed from one another only in the ratios of these elements present, there was no reason why they could not be changed into other materials by altering the amounts of these constituents. The doctrine of the transmutation of metals was perfectly logical under the prevailing thought. Attempts to convert lead into silver and brass into gold were acts of supreme sanity in those days. Not only was the science of chemistry, as it exists today, absolutely impossible under such environment, but the way was opened for all the quackery and imposition that characterized the alchemist of medieval times.

The Conception of Elements.—With the collapse, about the sixteenth century, of the old philosophy, men began to consider as elements those substances which they could not resolve into simpler materials. There were no longer four or five elements, but many, and each of them immutable, except as their properties were changed upon entering into combination.

When once the true elemental theory of matter had been established, chemical science found its first expression in the inquiry, “Of what elements do various substances consist?” From this impulse developed qualitative analysis—the original and, in certain respects, the most fundamental phase of the science of chemistry. After it came quantitative analysis, then inorganic chemistry, then organic chemistry, followed by physical chemistry, biological chemistry, and so on. History repeats itself in almost every piece of present-day research. When a new substance is isolated, it is first subjected to qualitative and then to quantitative analysis, before its reactions and applications are considered.

Notable Analysts.—A number of chemists have made memorable contributions to the science of analytical chemistry. Robert Boyle (1627–1691) invented the terms *analysis* and *reagent*, and

introduced a number of specific reagents, *e.g.*, Ca^{++} for SO_4^{--} , Ag^+ for Cl^- , etc. Scheele (1742–1786), the discoverer of chlorine, extended analytical methods, though his main work was in developing new reagents. Berzelius (1779–1848), of dualistic fame, developed blowpipe analysis, and two of his students, H. Rose and Fr. Wöhler, did important service in adapting qualitative methods to quantitative work. But two names stand out above the rest: Bergman (1735–1784), who substituted “wet methods” for the fire-assay procedures of the early analysts, and K. Remigius Fresenius (1818–1897), who did so much in the way of editing and codifying analytical methods. By way of recognition of the services of the latter, he has been called the *father of analytical chemistry*.

Assay Methods.—In the earlier days, chemical analysis was concerned largely with the analysis of ores, to determine what valuable metals they might contain. The most natural thing to do was to carry out a smelting operation on a small sample of the material. From these small-scale operations developed the fire methods that have been so important in the mineral industry. The ores are ground, mixed with various fluxes, and then smelted, *i.e.*, heated to the melting point. The nobler metals are reduced and separate, usually in a layer at the bottom of the melt; the baser metals are not reduced, but combine with the flux to form a dross, or slag. In later years, these smelting methods have been largely superseded by wet methods, in which the operations are carried out in water solution.

“Spot” and “Drop” Tests.—Some Austrian chemists—notably Pregl, Emich, and Feigl—have worked out a number of tests for cations that are highly specific and can therefore be applied directly on the original material. The reagents employed, however, are unusual; most of them are complex organic compounds. Such procedures are of no educational value to the elementary student in learning the fundamental processes of analytical chemistry. For the present, it seems better to restrict their use to advanced analysis, to be taken by students after they are familiar with organic chemistry.

Physical Methods.—Under this general heading will be included instrumental methods which do not involve chemical separations.

The most important contribution in this field is spectrum analysis, developed by Bunsen and Kirchhoff in 1860. Incandescent gases emit light containing characteristic wave lengths. By means of the spectroscope (page 425), this light may be broken down into its component colors, and these are recognized by the colors and positions of the lines produced. This method has been used to discover 11 new elements in the earth's crust and to study the chemical composition of the sun and stars (see pages 425 to 427).

The microscope has been used in identifying materials by their crystalline form. Chamot, at Cornell University, Ithaca, New

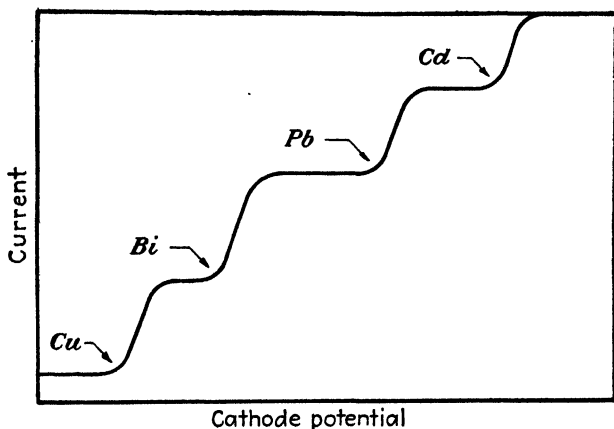


FIG. 1.—A polarograph.

York, has been the most conspicuous American in this field. Necessarily this field is limited, for not all materials can be brought into distinct crystalline forms. Microscopy is also used by the mineralogist in the study of the physical components of rocks.

X-rays have also proved a valuable adjunct to pure chemistry in detecting the physical components of mixtures. An unknown is identified by matching its X-ray pattern with those of known substances. While X-ray analysis is hardly to be regarded as an independent procedure, it is very helpful in clearing up points about which chemistry leaves us in doubt. For example, X-ray analysis shows very conclusively that the formula of calomel is Hg_2Cl_2 , and not HgCl .

In 1927, Allison introduced the magneto-optic procedure and announced the detection by its use of the new elements alabamine and virginium. This procedure is based upon the Faraday effect, *i.e.*, the rotation of the beam of polarized light upon passing through solutions placed in a magnetic field. Different solutions show different "lags" in responding to the magnetic effect, and these lags are determined by the ions present in the solution.

One of the latest instrumental methods for qualitative analysis is the polarograph, devised by Heyrovsky and his collaborators at the University of Prague. Various cations require different potentials for their discharge on the cathode. A cell is subjected to a slowly increasing voltage, and the current is plotted against the cathodic potential. When the potential reaches the discharge potential for a cation, there will be a sharp increase in the current at that point. Figure 1 shows the polarograph for a solution containing Cu^{++} , Bi^{+++} , Pb^{++} , and Cd^{++} .

In spite of all the clever devices of engineers, it seems likely that no general method will ever be worked out that will replace pure chemistry in qualitative analysis. Analysis probably always will be a chemical art.

CHAPTER II

SOLUTIONS

Almost all the reactions of analytical chemistry are "wet" reactions; *i.e.*, they consist in the action of solution upon solution, or of solution upon solid. "Dry" reactions are infrequent. Perhaps the most important is the ignition of a precipitate or residue. There are a number of reactions in which a gas appears to react with a solid; *e.g.*, HCl reddens blue litmus paper, and H₂S corrodes metals. Such reactions take place slowly, if at all, when gas and solid are perfectly dry. In general, it appears that water must be present to serve as a solvent for the reactants before any reaction will occur. A similar situation is found in the reactions between solids and solutions. The less the solubility of a solid in water, the less is its activity toward solutions. It seems probable that if a solid were absolutely insoluble in water, its activity toward solutions would become zero.

In order, then, to understand as fully as possible the mechanism of the reactions of analytical chemistry, a certain study of the properties of solutions should be made.

Definitions.—A solution is usually defined as a homogeneous liquid mixture whose composition may be varied within certain limits. The liquid involved is called the *solvent* and is generally present in excess. The other component is called the *solute* and may be a solid, a gas, or another liquid. The convention of calling the liquid the solvent is followed even for very concentrated solutions, where a very large amount of solid dissolves in a small amount of liquid. As an illustration of this unusual case, 4 or 5 g. of ZnBr₂ will dissolve in a single cubic centimeter of water. The terms *solvent* and *solute* become interchangeable for liquid mixtures, such as water and alcohol.

Besides liquid solutions, there are also gaseous and solid solutions. Any gaseous mixture will illustrate the first. Solid solutions may be illustrated by certain solid mixtures that are perfectly homogeneous physically; *e.g.*,

gold-silver alloys, mixtures of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and benzene and iodine at low temperatures. As in liquid solutions, the composition may vary within definite limits. It has been shown that solids may diffuse into one another. In brief, solid solutions have all the characteristics of liquid solutions except fluidity.

Saturated and Supersaturated Solutions.—A saturated solution is one that contains all the solute that it can hold at the given temperature in contact with an excess of the solid. If this solid phase is absent, a higher concentration may exist, called a *supersaturated solution*. The excess solute may be made to precipitate by introducing a small amount of the solid and shaking. In many cases, equilibrium is reached in a short time; in others, hours may elapse before the solute content is reduced to that of a saturated solution.

Supersaturated solutions are obtained by cooling solutions prepared at high temperatures out of contact with the solid solute or, chemically, by mixing two solutions that react to form the solute. A supersaturated solution of SrSO_4 may be prepared by mixing dilute solutions of SrCl_2 and H_2SO_4 . The precipitate forms slowly, and several hours are required for the completion of the precipitation. Supersaturated solutions are usually broken down by agitation and standing. In certain stubborn cases, it may be desirable to “seed” the solution with a small amount of the solid solute. This process is called *inoculation*.

Supersaturation brings about incomplete precipitation and is responsible for a number of errors in qualitative analysis.

Methods for Expressing Solubility.—At first thought, the simplest method for expressing the composition of a solution would be by relative weight of solute and solvent. For example, 10 g. of NaCl in 90 g. of water gives a 10 per cent solution (by weight). It does not follow, however, that 90 cc. of such a solution would contain 10 g. of NaCl . There is practically always a volume change when solutions are formed (see page 48). A more common method for expressing solubility is by a weight-volume relationship, *e.g.*, a solution containing 100 g. of NaCl per liter. This differs slightly in concentration from the preceding solution. The specific gravity of the latter is 1.066, so that its weight composition is 9.4 per cent NaCl . For dilute solutions the two methods give practically identical values.

The chemical unit of mass is not the gram but the *mole* (the molecular weight in grams). A *molar solution* is a solution containing 1 mole of solute per liter of solution.¹ Molar solutions are indicated in either of two ways: (1) By an *M* prefixed to the formula, fractional values being shown by the proper decimal fraction. To illustrate: 1.25 *M* H₂SO₄ contains 1.25×98 g. (1 mole) of anhydrous H₂SO₄ per liter of solution. (2) By the formula of the solute placed in brackets; *e.g.*, [H₂SO₄] = 1.25. The concentration of ions is generally expressed in the second manner. [SO₄[—]] = 0.12 means that a liter of the solution contains 0.12 gram ion (*i.e.*, 0.12×96 g., or 11.52 g.) of SO₄[—] per liter.

Another method for expressing concentration is in equivalents. An equivalent is the weight of a substance that will react with 1 g. of hydrogen, or with such amount of another substance as will react with 1 g. of hydrogen. A solution containing 1 equivalent per liter is called a *normal solution*. Normality is expressed by an *N* preceded by a numeral; *e.g.*, 0.2 *N* H₂SO₄ contains 0.2×49 g. (an equivalent), or 9.8 g. of pure H₂SO₄ per liter. Normal solutions are used chiefly in titration work in volumetric analysis.

Solubility Graphs.—A very convenient way for representing solubilities is by means of graphs (see Fig. 2). In this book, solubilities will be plotted as moles per liter on the vertical (ordinate) axis, and the temperatures (or other variable) on the horizontal (abscissa) axis. It is easy to obtain from these the solubilities for any required temperature or composition by interpolation.

Effect of Temperature on Solubility.—Increase in temperature usually favors increase in solubility, though there are notable exceptions. In some cases the solubility curves are steep, in others flat; some are straight, others curved. This variety of behavior should impress the student with the fact that there are

¹ Differing slightly from molar solutions are *molal solutions*, which contain 1 mole of the solute dissolved in 1 l. of the solvent, giving a final volume something greater than a liter. It follows that a molar solution is slightly more concentrated than a molal solution. Molar solutions are used in general and analytical chemistry, while molal solutions find their vogue in physical chemistry.

very dissimilar influences operating in solution. The whole phenomenon appears much too complex to be explained by any simple mechanism.

Mechanics of Solution and Precipitation.—Let us consider what happens when an excess of a solid—*e.g.*, rock candy—is placed in water. The solid dissolves very rapidly at first, depending on how finely it is divided, the rate of stirring, and so forth.

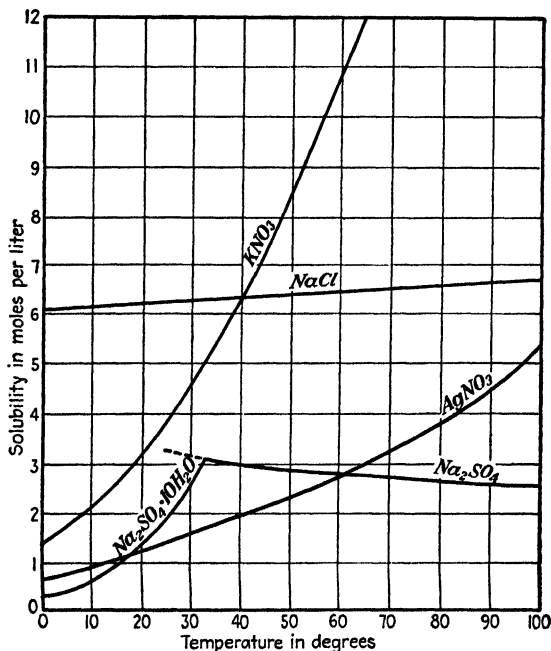


FIG. 2.—Solubility curves.

The speed of solution falls off rapidly and finally becomes zero. The solution is then saturated. The conditions affecting the rate of solution are significant: besides being influenced by the nature of the solid, the speed of solution varies directly as the exposed surface of the solid and inversely as the concentration of the solution next to the solid. Stirring reduces this local concentration and thereby facilitates solution.

A simple explanation of these effects is found in assuming that there are two actions in operation: *viz.*, solution and precipitation. The speed of solution is determined, for a given set

of substances at a definite temperature, by the surface exposed to the liquid. The speed of precipitation, on the other hand, is determined, not only by the exposed surface of the solid, but also by the concentration of the solution near the solid. When the rate of precipitation becomes equal to the rate of solution, so that they neutralize each other, the solution is saturated.

It was formerly thought that the solute dissolves until the solution is saturated and that then action ceases. It may be safely assumed that such is not the case. Suppose an irregular piece of rock candy, weighing, say 50 g., is suspended in a saturated solution of cane sugar. After standing for several weeks, the piece of rock candy will still weigh 50 g., but it is not the original piece. Instead of being irregular in shape, it has become an almost perfect four-sided prism. Evidently a give-and-take action has been going on during the period of standing. Jagged parts have dissolved off, and sugar has been deposited in the low places. This experiment was carried out in numerous cases in preparing the crystals of various chemicals exhibited at the Century of Progress Exposition in Chicago in 1933-1934.

The discussion of the mechanics of solution and precipitation will be resumed later, in the chapter on Equilibrium (pages 43-54). There the precipitation tendency will be interpreted in term of *osmotic pressure*, and the solution tendency in terms of *solution pressure*.

Effect of Particle Size on Solubility.—It is generally believed that small particles have a greater solubility than large ones. Hulett, at Princeton University, reported that BaSO_4 particles 0.0018 mm. in diameter have a solubility of 0.00229 g. per liter and that particles 0.0011 mm. in diameter have a solubility of 0.00415 g. per liter—almost twice as much. Similar increases in solubility have been found in CaSO_4 and HgO .

From this it would appear that fine particles have a higher speed of solution than large particles. This may be explained in two ways: (1) The speed of solution is determined by the amount of surface exposed to the solution. Since, for a given weight of solid, the surface increases directly as particle size diminishes, we would expect just the increase mentioned above. (2) Another possibility is that solution pressure is greater for edges and points than for flat or hollow surfaces. This would explain why irregular particles should tend upon standing to

pass over into symmetrical crystals. At any rate, upon digestion, large crystals do grow at the expense of small ones. For this reason solutions filter better after standing.

Most precipitates are mixtures of particles of unequal sizes. The very small ones may tend to "run through the filter" or else plug up its pores so that filtration proceeds very slowly. Upon standing, the small particles, by reason of their greater solubility, go back into solution and reprecipitate on the larger ones. Stirring favors crystal growth because the high concentrations forming about the small crystals are brought into contact with the larger particles, toward which they are supersaturated. Heating also favors crystal growth because it speeds up both solution and osmotic pressures.

This principle of solubility varying inversely with particle size is not accepted by all writers. Some seem to prefer to explain crystal growth by some sort of coalition of solid particles.

Characteristics of Solutions.—It may be worth while to summarize some of the most distinctive properties of solutions.

Homogeneity.—So far as instrumental evidence goes, solutions behave like liquids, or mixtures of liquids. They are "optically empty"; i.e., a beam of light passes through them without leaving a trail. On the other hand, suspensions, when illuminated by a beam, become luminous, owing to reflection of light from their surfaces (the Tyndall effect).

Nonsettling.—In a mobile system, like a solution, any difference in density in the ingredients should manifest itself in a tendency toward settling. Some have assumed that the kinetic motion of the particles would result in a uniform dispersion of a heavy solute throughout the whole solution. This is not theoretically correct. Neglecting the effect of gravity, the resultant of the random motions of the particles of a solution is zero, and no settling should take place. But since the free motion of the particles provides no component to balance gravity, a settling of the heavier particles is to be expected. However, there is no evidence of such behavior. Samples of ocean water from various depths have been analyzed, and for the same place the concentration of dissolved matter is constant, except at the surface, where it is affected by evaporation, rainfall, waves, etc.

Diffusion.—The components of a solution—both solute and solvent—seem to be in continuous motion. This is shown in several ways. If a gelatin capsule containing a water-soluble substance—mercurochrome, for example—is dropped into a cylinder of water, the dye will gradually diffuse until it reaches the top of the cylinder. Doubtless, if the experiment were allowed to stand long enough, the distribution would become perfectly uniform. Evidently the dye particles are in motion, by virtue of which they distribute themselves throughout the whole solution.

The molecules of the solvent may be shown to be in motion another way. If a suspension of a colloid, such as the resin

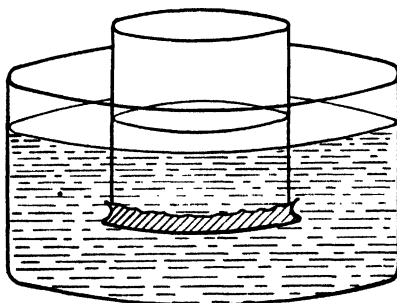


FIG. 3.—Dialysis cell.

gamboge, is examined under the microscope, the particles show a peculiar, irregular motion, called the *Brownian movement*. This motion, it is generally agreed, is due to the bombardment of the colloidal particles by the molecules of the solvent.

Dialysis and Osmosis.—Some materials are permeable to pure water but are impermeable to certain solutes. For example, parchment paper, collodion, and certain animal membranes permit the passage of water and certain small-sized molecules but not of bulky molecules. Such filters or membranes are said to be *semipermeable*.

If a solution containing salt and sugar is placed in a parchment bag and the bag is placed in a vessel of pure water, the salt will pass through the membrane, but the sugar will be retained. This process is called *dialysis* and is sometimes used for removing salts from colloids. One form of apparatus is shown in Fig. 3. If the water in the outer vessel is continually replaced—*e.g.*, if

the bag is placed in a trough of running water—the salt can be completely separated.

A more striking experiment is known as *osmosis*. A solution of sugar is introduced into a vessel separated from pure water by means of a semipermeable membrane (Fig. 4). A good membrane for qualitative purposes is a diffusion thimble which is tightly tied to the flared end of the glass tube. After standing some hours, the solution will be found to have risen in the tube, showing that water has passed from the beaker into the solution.



FIG. 4.—Osmosis.

The explanation is as follows: The sugar molecules are too large to pass through the membrane and so are retained in the bulb. The water molecules are smaller and are able to diffuse through the membrane. Now the sugar *dilutes* the water within the bulb; therefore, relatively fewer molecules of water strike the inside surface than strike the outside surface, and hence more water diffuses inward than outward. This diffusion will continue until the hydrostatic pressure within the tube is great enough to stop the influx of water. This pressure is called *osmotic pressure*, and indirectly it is proportional to the concentration of the sugar in the solution. The popular notion that the sugar is directly responsible is not accurate.

These experiments prove that diffusion in solution is due not only to the motion of the particles of the solute but also to that of the particles of the solvent. Really the latter is probably the more effective of the two.

Boiling-point and Freezing-point Behavior.—Pure water containing a suspension of an insoluble solid, such as clay, boils at 100° (at 760 mm.) and freezes at 0° . On the other hand, the boiling point of the solvent is always raised by the presence of a (nonvolatile) solute, and the freezing point is lowered. These effects will be used later to calculate the degree of ionization of a solute.

Conductivity of Electricity.—Perhaps the most important characteristic of solutions is that certain of them (though not

all) conduct the electric current. Since the solute undergoes decomposition, the process is called *electrolysis*, and such solutions are called *electrolytes*. The solutes, in the pure form, are called *ionogens*. The behavior of electrolytes in this respect is the basis of the ionization theory (page 55).

Analogy between Liquid and Gaseous Solutions.—Ordinary membranes are not strong enough for quantitative measurement of osmotic pressures. Decidedly the most useful membranes for this purpose are formed by placing a CuSO_4 solution inside of an unglazed porcelain cylinder and a $\text{K}_4\text{Fe}(\text{CN})_6$ solution on the outside. These solutions diffuse into the porous walls; and, where they meet, a membrane of cupric ferrocyanide, $\text{Cu}_2\text{Fe}(\text{CN})_6$, is formed. This membrane not only will retain ionic materials but also will withstand considerable pressures. By means of these membranes, the botanist Pfeffer and others have been able to measure osmotic pressures with considerable accuracy.

Van't Hoff has pointed out a parallelism between osmotic and gaseous pressures. At 0° , molar solutions of nonelectrolytes have an osmotic pressure of 22.4 atm.—just the same pressure as 1 mole of gas in a volume of 1 l. at 0° . Further, osmotic pressures increase $\frac{1}{273}$ per degree of temperature, in strict analogy to Charles's law for gases. Hence solutions are analogous to gaseous mixtures, and their behavior may be expressed by the same equation $PV = RT$, where P is the pressure in atmospheres, V is the volume containing 1 mole of the solute, T is the absolute temperature, and R is the gas constant (0.0813 l.-atm.). This generalization is known as *van't Hoff's law*.

The approximate nature of this generalization must be conceded. No gas obeys the gas law exactly, and the deviation of solutions from the van't Hoff law is much greater. These differences are too great to be due to experimental error.

Are Solutions Physical Mixtures or Chemical Compounds?—There are two very different conceptions as to what happens to a solute when it dissolves. According to one group, there is no sharp difference between solubility and insolubility. It is merely a question of particle size. If the particles are large enough to be visible to the unassisted eye, we have a precipitate; if they are so small that they are visible only by means of a

microscope, we have a sol (see page 24); if smaller still, we have a solution.

The more chemically minded are not satisfied with this conception of solutions. They prefer to think that the solute combines with the solvent, forming a pseudochemical compound of some kind.

These two theories of solution may be outlined as follows:

The Physical Theory of Solutions.—Physicists have wished that solutions were analogous to gaseous mixtures. They like to think of the solvent as being an inert atmosphere or a dead space surrounding the particles of a highly dispersed solute. A modified set of gas laws could then be applied to the calculation of the properties of solutions. Such a theory might be called an *atmosphere theory of solutions*.

Much time and work have been spent in trying to establish this parallelism between liquid solutions and gas mixtures, with no other result than bringing out small but appreciable differences. Certain inferences that might be drawn turn out to be incorrect. For example, if the solvent were nothing but a diluting agent, then solutes should be equally soluble in all solvents, or even in a vacuum. On the other hand, the fact remains that solutions, particularly at low concentrations, do approximate the behavior of mixtures, and this fact does facilitate many of our calculations. Still, the inexact behavior is evidence that some other effect is superposed upon that of simple dispersion.

If solutions are physical mixtures, their properties should be additive; *i.e.*, an average of the properties of the components. By properties is meant such characteristics as volume, heat content, odor, color, conductivity of heat and electricity, and melting point. When two or more substances are mixed and there is a definite change in the summation of these properties, a chemical change is said to have occurred. In solutions, physical mixtures are only approximated. There are, probably in all cases, changes in volume, heat content, conductivity of heat, and melting and boiling points. To illustrate: There is an absorption of heat when NH_4Cl dissolves in water, and an evolution of heat when H_2SO_4 dissolves in water. In the first case, the volume is greater than that of the solvent and solute, and less in the second. In both cases, the electrical conductivity is far greater than would

be expected from the law of mixtures. At very low concentrations (or high dilutions), the properties of solutions are practically additive.

Illustration.—The deviation of solutions from the law of mixtures may be illustrated by a solution of 1 cc. of NaCl in 10 cc. of water. The density of NaCl is 2.163; and of water, 1. According to the law of mixtures, the density of the solution should be: $(1 \times 2.163 + 1 \times 10) \div 11$, or 1.105. The actual density is 1.056. Again, if the NaCl is to be considered inert—just like a suspension of clay—the water should have a vapor pressure of 760 mm. at 100° and therefore should boil at 100°; if the salt is to be considered as fused (!), so as to form a true liquid mixture with water, the vapor pressure of the mixture should be $\frac{10}{11}$ of 760 mm., or 691 mm., and the solution should boil at about 103.2°. The fact is, it boils at 101.4°. In a similar way, it might be shown that other properties deviate from the ideal behavior.

Figure 5 shows the boiling points of solutions of ethyl alcohol and water at 760 mm. Ethyl alcohol boils at 78.4° and water at 100°. For intermediate compositions, the boiling

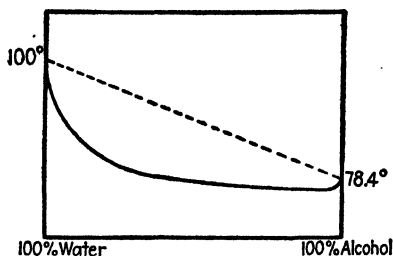


FIG. 5.—Boiling-point curve for mixtures of ethyl alcohol and water.

point is given by the solid line. The broken line represents the theoretical boiling points, assuming a truly physical mixture. It is interesting to note that 96 per cent alcohol has a lower boiling point than any other composition.

The Solvation Theory.—Most writers now think of solution, not as a physical change, but as a pseudochemical change. The solute and the solvent combine to form a loose compound called a *solvate*. The general phenomenon is called *solvation*. When the solvent is water, the solvates are called *hydrates*, and the general phenomenon is called *hydration*. Solution differs from ordinary chemical combination in that the solvates are not very stable and may have varying composition.

The principal arguments in support of the solvation theory may be listed thus: (1) The solute, upon going into solution, takes

on a new set of properties. It changes from solid to liquid; besides this, there are changes in density, index of refraction, and even in color. (2) Heat is evolved or absorbed upon passing into the dissolved state, possibly in all cases. (3) The properties of solute and solvent are not additive. The law of mixtures does not hold for volume, optical properties, electric properties, etc. (4) In many cases, soluble materials are known to form compounds with the solvent. H_2SO_4 forms H_6SO_6 , NaCl forms $\text{NaCl}\cdot 2\text{H}_2\text{O}$, and so on. As a rule, substances that show considerable disposition to form hydrates are highly soluble; however, there are many exceptions.

Exercises

1. Distinguish between a 10 per cent volume solution and a 10 per cent weight solution.

2. By means of the law of mixtures, calculate the density of the solution obtained by dissolving 1 cc. of solid ammonium chloride in 9 cc. of water. The density of solid NH_4Cl is 1.536. (The experimental density is 1.0286.)

3. How would you prepare 0.8 M HCl from 1.25 M HCl ?

4. What weight of 95 per cent H_2SO_4 would be used in preparing a liter of 3 M H_2SO_4 ? What weight of water would be required, if the density of 3 M H_2SO_4 is 1.19? *Ans.*: 309.5 g., 880.5 g.

5. Calculate the molar concentration of a solution containing (a) 20.7 g. of $\text{Pb}(\text{NO}_3)_2$ per liter, (b) 40 per cent (by weight) HCl per liter, (c) 10 per cent HNO_3 that has been diluted with 1.5 volumes of water.

6. What is the concentration of the NaCl in the solution formed by neutralizing 1.2 M NaOH by 0.8 M HCl ?

7. What is the molarity of 3 per cent H_2O_2 solution? Why is this concentration called "10-volume peroxide"?

8. Three cubic centimeters of 6 M HNO_3 is added to 2 cc. of 15 M NH_4OH , and the mixture is diluted to 40 cc. What will be the various concentrations of the materials present in the mixture?

9. Forty cubic centimeters of 6 M HCl is mixed with 60 cc. of 15 M NH_4OH . Calculate the molarity of the constituents of the resultant mixture.

10. Twenty-five cubic centimeters of a concentrated oxalic acid solution containing 160 g. of $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ is diluted to 40 cc. What is the final molarity?

11. A mixture of 4 cc. of 0.3 M $\text{Hg}_2(\text{NO}_3)_2$ and 5 cc. of 0.2 M $\text{Pb}(\text{NO}_3)_2$ is diluted to 50 cc. What is the molarity of each of the salts in the resultant mixture?

12. In general, is the ratio of solution pressure to osmotic pressure constant, or does it vary with the temperature?

13. Refer to a handbook and choose some solute (*e.g.*, CuBr_2), and use it to explain your views as to whether solution is a physical or chemical change.

14. Anhydrous $\text{Mg}(\text{ClO}_4)_2$ dissolves in water, the system showing a considerable shrinkage. Would you expect this salt to have a positive or negative heat of solution?

15. Exactly speaking, are volumes truly additive?

16. Distinguish between molar and molal solutions.

17. From Fig. 2, estimate the solubility of AgNO_3 in water for the temperatures 10° , 25° , and 50° .

18. Explain why pulverizing a solid increases its speed of solution.

19. What appears to be the relation between the curvature of the surface of a solute and its solution pressure?

20. State van't Hoff's law.

21. Define and illustrate the solvation theory.

22. Which is directly responsible for osmotic pressure, the solute or the solvent? In a setup using a membrane, which way does it bulge, toward the dilute or the concentrated solution?

23. How would you determine whether a five-cent coin is a solid solution or not?

24. Prove by geometry that a solid should dissolve twice as fast after being ground to particles of one-half the original diameter.

CHAPTER III

THE COLLOIDAL STATE. MECHANICS OF PRECIPITATION

Why are some precipitates crystalline and easy to filter, while others are gummy and hard to filter?

Graham, in 1862, thought that he had found the answer to this question when he came to the conclusion that some substances are by nature crystalline and others by nature colloidal (gluelike). This classification of substances into *crystalloids* and *colloids* is in general a useful one, but it is incorrect in one fundamental point. The nature of a precipitate is now known to be determined, not by its composition, but by its method of formation. For example, sodium chloride, NaCl , is precipitated from a salt solution by means of concentrated HCl in a distinctly crystalline form; but if precipitated by alcohol, the product is gummy and amorphous. Again, silicic acid, H_2SiO_3 , is precipitated from a solution of alkaline silicates by acids as a colloid, resembling starch in its consistency; but when "laid down" in the earth's crust from terrestrial water, it takes the form of crystals of quartz, several centimeters in length. Silver chloride, AgCl , is described in most textbooks as "curdy"; yet if it is dissolved in concentrated HCl , and the latter is allowed to evaporate very slowly—months are required—beautifully crystalline AgCl is obtained. It appears that nearly all inorganic precipitates are crystalline if they are allowed to form slowly enough.

THE COLLOIDAL STATE

Many of the precipitates with which the analytical chemist has to work are colloidal. As such they are hard to filter and wash. It is important to know how to handle these precipitates, and for this reason certain aspects of the colloidal state call for consideration.

Definitions.—Colloidal chemistry has an extensive nomenclature. Some of the terms used are defined in the following:

Colloidal solutions (so-called) are not true solutions, but mixtures. Close examinations shows that they are not homogeneous but consist of suspensions of solid or liquid particles in a liquid. Such a mixture is known as a *disperse system*; the liquid (usually water in analytical work) is called the *dispersion medium*, and the colloid the *disperse phase*. This disperse phase may be roughly classified as suspensoid or emulsoid.

Suspensoids are solids, *e.g.*, the mud in muddy water. They must be very insoluble, for they do not affect the properties of the dispersion medium. For example, they do not lower its freezing point or raise its boiling point. There is no noticeable increase in the viscosity. They are simply suspensions. After drying, suspensoids usually do not revert to the colloidal form. For this reason, they are said to be *irreversible*, or *lyophobic* (solution hating). Ferric hydroxide, $\text{Fe}(\text{OH})_3$, is an example of an irreversible suspensoid. Upon drying, it forms $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, which will not resume the gelatinous form upon adding water. Suspensoids are generally electrically charged and will slowly migrate toward the anode or the cathode when brought into an electrostatic field (cataphoresis). Usually suspensoids are inorganic in nature.

Emulsoids are jellylike in consistency and approximate the liquid state, *e.g.*, gelatin, jellies, mucilage, etc. In some cases, they are definitely liquids, as in milk, which consists of droplets of fat suspended in an aqueous solution. They increase the viscosity to a marked degree; for example, a 4 per cent agar-agar solution sets to a stiff jelly. In most cases, dried emulsoids will recombine with water and return to the colloid form. They are therefore said to be *reversible*, or *lyophilic* (solution loving). Most emulsoids are organic in composition, and many of them have never been separated in the crystalline form.

Many substances are hard to classify under the suspensoid-emulsoid system. Silicic acid at room temperature, for example, is definitely an emulsoid, forming a translucent gel that resembles gelatin. Upon careful drying it forms *silica gel*, which may be used as a drying agent. On the other hand, if silicic acid is heated at 120° for a short time, it loses its lyophilic properties and acts like an irreversible suspensoid.

Suspensoids are met more frequently in analytical work than are emulsoids, but both deserve attention.

Various names are given to colloidal materials according to the size of the particles. If they are large enough to be seen by the unassisted eye, they are called *precipitates*; if visible under the microscope, *suspensions*; if submicroscopic, *sols*. The sols in aqueous systems are sometimes called *hydrosols*.

A description of a sol might be helpful. If an aqueous solution of arsenious oxide, As_2O_3 , is saturated with H_2S , the liquid becomes yellow, but no precipitate appears. Upon standing, the mixture becomes turbid, and later a yellow precipitate of As_2S_3 separates. If HCl or other electrolyte is added, As_2S_3 is thrown down immediately as a gummy, yellow precipitate. This illustrates the transition from sol to suspension to precipitate.

The very small dimensions of colloidal particles have called for some new units of magnitude: the *micron*, μ , which is one-thousandth of a millimeter, *i.e.*, 0.001 mm.; and the *millimicron*, $\mu\mu$, which is one-millionth of a millimeter, or 0.000001 mm. The following are rough estimates of the diameters of colloids and molecules:

Suspensions.....	$>0.1 \mu$
Sols.....	$0.1 \mu-1 \mu\mu$
Molecules.....	$<1 \mu\mu$

Many colloids are dispersed by ions or other colloids. For example, when AgNO_3 reacts with a chloride in the presence of gelatin, a practically clear liquid results. The AgCl is said to be "protected" by the gelatin; this dispersion of colloids is also called *peptization*, or *deflocculation*. Likewise, sols may be protected by adding lyophilic colloids, *e.g.*, silver sols, like argyrol, by proteins.

Structure of Dispersoids.—Many suspensoids, judging by the small residue left upon drying, are very highly hydrated. Probably each particle is surrounded by an envelope of water, which protects it against coalescing with other particles. As stated above, these suspensoids are not in true solution, even though they appear transparent. Judged by their behavior, suspensoid systems are definitely two-phase systems.

Emulsoids may form gels (jellies), in which the colloid takes the form of a spongelike skeleton. This gelatination increases the viscosity of the system tremendously but offers little resistance to ionic movement within the dispersion medium. For example, the presence of gels reduces the electrical conductivity of electrolytes very little. From the physical point of view, gels look and behave just like very viscous liquids.

X-ray examination of inorganic suspensoids shows that their basic structure is generally crystalline. Their amorphous appearance is due to the fact that the particles—like brick piled at random—have no definite arrangement with respect to each other. This random arrangement is probably favored by the high hydration of the particles.

Properties of Colloids.—The following properties of colloids are of interest to the analytical chemist:

Inhomogeneity.—To the unassisted eye, many colloidal systems (*e.g.*, sols and emulsions) are homogeneous, and this apparent homogeneity is responsible for their being frequently called *colloidal solutions*. “Pseudosolutions” would be a better name. While suspensions have certain properties suggesting solutions, the following facts indicate that the disperse phase is really a finely divided suspension floating in the dispersion medium. (1) Colloidal systems show the Tyndall effect. If a beam of light is passed through a sol (*e.g.*, As_2S_3) in a dark room, it leaves an illuminated trail, just as a beam of light shows the dust in the air of a room. This phenomenon is due to the reflection of light from the surfaces of the submicroscopic particles. (2) The freezing point of the system is that of the dispersion medium, showing that its concentration has not been affected by a dissolved solute. Similarly, the boiling point and osmotic-pressure behavior indicate that the system is a physical mixture. (3) Colloids of the larger dimensions are visible under the microscope. (4) Colloids do not diffuse through membranes, presumably because their particles are larger than the pores of the filter.

Electric Charges.—Most gels are electrically neutral, but sols are electrically charged. This is shown by their migration when placed in an electrolytic circuit. In Table 1, suspensoids are classified as positive or negative, according to the nature of the

charge. These charges vary with the dispersion medium. For example, the charge on most colloids is reversed when turpentine is used instead of water as the dispersion medium.

TABLE 1.—ELECTRIC CHARGES ON AQUEOUS SUSPENSIONS

Positive Colloids	Negative Colloids
Metallic hydroxides	Metallic sols
Albumen	Metallic sulfides
Many dyes	Silicic acid
	Stannic acid
	Silver chloride
	Gums
	Starch
	Certain dyes

The source of these charges is not definitely known. Possibly they are due to adsorption of ions from the solution: *e.g.*, metallic hydroxides tend to adsorb H^+ ions, thereby becoming positive; and metallic sulfides adsorb OH^- or SH^- ions, thereby becoming negative. There is indication that other cations and anions are also adsorbed.

Coagulation.—Colloidal suspensions may be made to coagulate in various ways. Certain of them—particularly certain of the organic gels, such as albumen—may be precipitated by heat. Others are precipitated by the introduction of new solvents, such as alcohol. In analytical procedures, the most important method of precipitation is by the addition of electrolytes. The charges on the ions of the electrolyte in some way neutralize the charges on the colloid, so that the particles can coalesce. It is not surprising to find that the precipitating ion is “carried down” during the precipitation in a form that is very hard to remove by washing. Positive colloids are precipitated by negative ions, and negative colloids by positive ions. The coagulating power of an ion is in some way related to its valence. For example, silicic acid is a negative colloid and therefore coagulated by cations. In the precipitation of H_2SiO_3 , Mg^{++} ions are more effective than Na^+ , and Al^{+++} ions more effective than Mg^{++} . The effectiveness of the precipitant, it will be seen, increases with its valence (the Schulze-Hardy law). This rule is only roughly valid. The coagulating power of the same concentration of ions of the same valence is not the same; *e.g.*, the negative

colloid, As_2S_3 , is precipitated more readily by $M \text{Mg}^{++}$ than by $M \text{Ca}^{++}$.

Sometimes colloids precipitate each other, *e.g.*, ferric hydroxide (positive) and arsenious sulfide (negative).

Heat alone is seldom sufficient to coagulate a colloid, but it is usually very helpful. It probably speeds up the action of other agencies and perhaps favors the solution of the smaller particles and their reprecipitation on larger particles.

Adsorption.—As has been stated above, colloids have a marked property of carrying down in their coagulation electrolytes present in the solution, particularly the ions of the opposite sign. The complexes formed by the coalescence are rather stable, for it is difficult to wash the colloids free from the contaminating electrolyte. The impurity is usually supposed to be held on the surface of the colloid (adsorption), but there is no reason why it should not also be included within the colloid (inclusion), especially if the electrolyte was present when the colloid was precipitated.

Peptization by Washing.—If it is attempted to wash a coagulated colloid until it is free from adsorbed impurities, the colloid is apt to be peptized and to “run through the filter.” Consequently, colloidal precipitates are washed with solutions of electrolytes, and not with pure water. Usually HCl and NH_4Cl are the electrolytes used, since, when necessary, they are easily expelled from residues by gentle ignition.

Summary.—The proper technique for handling precipitates that tend to become colloidal is so important that the general procedure may be restated as follows: (1) Colloids should be precipitated from hot solutions. (2) Suitable electrolytes should be added to bring about coagulation. (3) The precipitant should be added slowly. (4) The mixture should be stirred during the precipitation. (5) It is desirable to let the precipitate stand (preferably, hot) for some time before filtration. (6) Suction filtration frequently is not helpful. (7) The wash water should be hot and should contain an indifferent electrolyte.

Lakes.—Colloidal metallic hydroxides have the property of combining with certain soluble dyes, forming precipitates which, in most cases, are highly colored. These precipitates are called *lakes* and constitute the permanent colors in the dyeing of calico.

The hydroxide is called a *mordant*, since it precipitates the dye in a water-insoluble form within the fibers of the cloth.

The nature of the complex formed when a dye combines with a metallic hydroxide is not fully understood. In some respects, the action appears to be physical (adsorption). For example, dyes are usually negative colloids, and metallic hydroxides are positive colloids; these neutralize each other, causing mutual coagulation. On the other hand, negative dyes do not form lakes with negative colloids, as H_2SiO_3 . In other respects, lake formation seems to be chemical. The hydroxides involved are basic, and the dyes have acidic groups. Colored compounds without acidic groups do not form lakes. Lakes are therefore saltlike, and their failure to hydrolyze shows their high insolubility. Another evidence of chemical combination is that the color of the lake is not a blend of the color of the dye and the hydroxide. For example, the yellow dye alizarin forms a red lake with white $\text{Al}(\text{OH})_3$ and a purple lake with brown $\text{Fe}(\text{OH})_3$. Green $\text{Cr}(\text{OH})_3$ forms with the red dye chromotrope a blue-to-black lake, and with the red dye, eriochrome azurol, a blue lake.

Lake formation is used as a confirmatory test for certain ions, particularly Al^{+++} (page 244) and Mg^{++} (page 303). It should be kept in mind that there are many interferences with lake tests, so that it is hardly permissible to use them on original unknowns or mixtures.

THE MECHANISM OF THE FORMATION OF PRECIPITATES

Frankly, the actual steps in precipitate formation, starting with the ions and ending with the precipitate, are unknowable. Both ions and molecules are too small to be detected by any physical means—for example, the microscope—and all that can be done is to speculate as to what happens. However, if a theory can be advanced that will picture the general phenomenon of precipitation in a lifelike way, it should be helpful in working out the technique in manipulation. Such a theory should not only be simple, but it should also be reasonable and, if possible, seem probable. The following is a modification of a theory proposed by von Weimarn to explain the formation of colloidal precipitates.

Suppose two solutions are mixed, bringing together the cation and the anion of an insoluble compound. Owing to the high mobilities of the ions, there will be frequent collisions, and molecules will be formed rapidly. If these molecules are not precipitated as fast as they form, a supersaturated solution will result. Now the molecules in supersaturated solutions are supposed to be highly hydrated, and in case of forced precipitation the *primary particles* that separate will carry envelopes of water. These primary particles do not have time to arrange

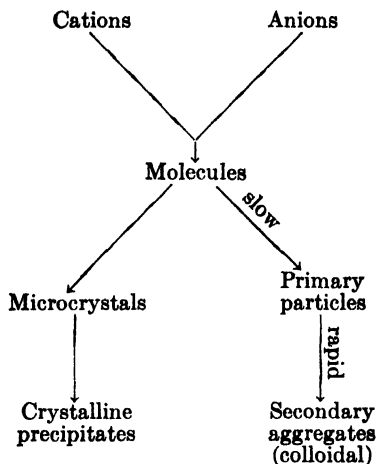


FIG. 6.—Precipitate formation.

themselves in an orderly fashion, even if the hydration envelopes permitted. The result is a jumble of *secondary aggregates*, more or less gelatinous in nature. On the other hand, suppose that the molecules formed are fairly soluble, so that no high degree of supersaturation is necessary. The molecules will then have time to lose their water of hydration and to find a definite place in the lattice of a crystal already in process of construction. In brief, colloidal formation of otherwise crystalline materials is due to a hurried, pell-mell form of precipitation and is especially characteristic of substances of high insolubility. This theory is represented in diagrammatic form in Fig. 6.

CHAPTER IV

THE OPERATIONS OF ANALYTICAL CHEMISTRY

All too frequently, students do not appreciate the importance of the technique employed in qualitative analysis. It should be remembered that, almost always, errors are due to lapses in technique. The following discussion is therefore timely.

TYPES OF SEPARATIONS

As a rule, an ion must be separated from other ions before the identification test can be applied. Qualitative analysis, then, involves two steps: (1) separation and (2) recognition. The first step is realized by converting the ions of the mixture into different physical forms, or phases, which may be separated by proper physical means. These separations may be classified as follows:

1. Gas from gas.
2. Gas from liquid.
3. Gas from solid.
4. Liquid from liquid.
5. Solid from liquid.
6. Solid from solid.

1. Gas from Gas.—Sometimes two gases are separated by their difference in speed of *diffusion* through a porous medium, e.g., NH_3 from HCl in Pebal's celebrated experiment on the dissociation of NH_4Cl by heat. In the manufacture of oxygen from air, on the other hand, the separation is not that of a gas from a gas but a gas (nitrogen) from a liquid (oxygen). Diffusion is not a standard procedure in analytical work. The two gases must differ considerably in density for the procedure to be efficient. Chemical methods are much more satisfactory.

2. Gas from Liquid.—The general procedure is recognized as *evaporation*, of which distillation and sublimation are special forms. When the gaseous phase is condensed to a liquid in a separate vessel, the action is called *distillation*; when it condenses

directly to a solid, it is called *sublimation*. These special forms are used extensively in the analysis of organic materials but seldom in inorganic analyses.

Strictly speaking, the separation of a gas from a liquid is an easy process. All that is necessary is to displace it by an inert gas. Sometimes there is considerable difficulty in making the material pass from the liquid to the gaseous phase. For example, it takes prolonged boiling to expel SO_2 from an aqueous solution. HCl cannot be completely separated from water in this way.

3. Gas from Solid.—As in the preceding case, this separation depends on the diffusion of the gas. In case the volatile substance is a gas at the prevailing temperature, the reaction might be expected to proceed spontaneously. Such is not always the case. Certain solids adsorb gases very strongly. For example, both heat and reduced pressure are necessary to “outgas” gases from charcoal.

This process may involve the vaporization of a liquid, as when a wet precipitate is dried by heating; or the vaporization of a solid, as when NH_4^+ salts are removed in Group V mixtures by ignition. In both cases it should be noticed that the volatile material is separated in the form of a gas, and not as a liquid or solid. Another illustration is the test for NH_4^+ with CaO or NaOH . Gaseous NH_3 is formed and is expelled by gentle heating.

4. Liquid from Liquid.—If two liquids are miscible with each other, they may be separated by removing one of them by means of a solvent insoluble in the other liquid. The process is called *extraction*. For example, if an aqueous solution of bromine is shaken with carbon tetrachloride (which will not mix with water), most of the bromine will pass into the latter solvent. This follows since bromine is much more soluble in carbon tetrachloride than in water. Suppose that equal volumes of solution and carbon tetrachloride are used, and that bromine is twenty times as soluble in the latter as in the former. When equilibrium is reached, the Br_2 concentrations will be in the ratio 20:1. That is, $\frac{20}{21}$ will be extracted, and $\frac{1}{21}$ will be left. If the carbon tetrachloride solution is now drawn off by means of a separatory funnel (Fig. 7) and the extraction repeated with a second volume of CCl_4 , the amount of Br_2 left in the water

will be $\frac{1}{21}$ of $\frac{1}{21}$, or $\frac{1}{441}$ of the original amount of bromine. In practice, extraction seldom attains this theoretical efficiency.

The equilibrium involved in extraction will be further considered in the chapter on Equilibrium (page 45).

5. Solid from Liquid.—The most general procedure for separating two ions is to precipitate one of them and then separate the precipitate from the solution. This separation of solid from liquid is, on account of its extensive use, the most important type of separation. There are two forms, *viz.*, *filtration* and *decantation*.

Filtration.—In this procedure, the mixture of solid and liquid is placed on some medium that will retain the solid but allow the liquid to drain through. The most common of these mediums is filter paper, made from carefully purified cellulose. Asbestos is used for mixtures that would attack paper, *e.g.*, mixtures containing strong oxidizing agents, such as $\text{MnO}_2 + \text{H}^+$ or $\text{H}_2\text{Cr}_2\text{O}_7$.

Decantation.—Decantation consists in pouring off the clear supernatant liquid, so as to leave the precipitate in the original vessel. It is satisfactory only in cases where the precipitate settles well. Decantation is frequently combined with filtration, particularly when the precipitate tends to clog the paper. In the latter case, the precipitate is allowed to settle, and the solution is decanted on to the paper, leaving behind

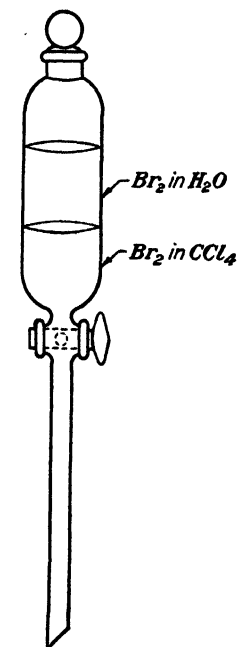


FIG. 7.—Separation of bromine from water in a separatory funnel by means of carbon tetrachloride.

as much of the precipitate as possible. Filtration proceeds rapidly during the first stages of the operation, and in this way much time is saved.

As will be seen later, neither filtration nor decantation gives a complete separation of liquid from solid, because solids always retain some of the liquid (*adsorption*).

6. Solid from Solid.—In earlier analytical procedures there were a number of methods for separating solids from solids,

depending on such properties as density and magnetism. The separation of gold from sand in the panning process was based on differences in density; the lighter sand was washed away from the heavier gold. A number of modern industrial separations also depend upon difference in density, as when a light material is separated by means of air flotation. There are other procedures of the "float-and-sink" type, as when sulfides are separated from siliceous materials by means of foam flotation. Iron is sometimes removed from mixtures by means of magnets, as in working up monazite sand.

The most common application of this principle in analytical chemistry is a mechanical separation of a mixture of particles of fair size and distinctive appearance. For example, certain mixtures may be separated into their components by means of forceps.

Separation of Colloids from Solutions.—There is one important separation that is sometimes used in analytical chemistry which is hard to classify under the above system. There are certain mixtures, like metallic sols (colloidal silver, for example), which will pass through filter paper unchanged; but if the same mixture is placed within a vessel made of parchment and surrounded by running water, the sol will be left within the vessel, while ordinary salts diffuse through the parchment. We like to explain this by assuming that the colloidal particles are really in the solid form but are of suboptic dimensions. As was seen in the discussion of osmosis (page 16), a similar separation takes place within a sugar solution, and that calls for the embarrassing assumption that sugar is not truly soluble—just a solid dispersed in water (see Colloids, page 24).

The removal of colloidal materials by active charcoal is another phenomenon that is hard to explain.

Completeness of Separation.—Accuracy in analysis requires that all separations should be as complete as possible, so as (1) to avoid losses of ions before they are tested for, and (2) to prevent interferences in the tests for other ions. It is easily seen that an ion whose test is made on a filtrate obtained after a number of operations (a Group V cation, for example) is liable to be lost unless special care is taken to wash out the

amount of this ion adhering to the precipitate in each filtration. Furthermore, ions not washed out of precipitates may interfere with tests made on these precipitates.

Precipitation.—Good students will soon learn that there is an art in carrying out a precipitation, even though the same procedure cannot be used in all cases. An excess of the precipitant should never be “dumped” into a solution. Rather, it should be added slowly, and each addition should be followed by shaking or stirring. If a precipitate appears, it should be allowed to settle, and a drop or so of the reagent added to the supernatant clear liquid to test for completeness of the reaction. In the case of nonsettling precipitates, the mixture must be filtered and a test made on the filtrate.

When it is permissible, precipitation is carried out in hot solutions. The mixture is allowed to stand until cool before filtering. The precipitates obtained by observing these precautions of slow addition of reagents, stirring, digestion, etc., are more crystalline and filter and wash better.

The student is warned against the assumption that precipitations are practically instantaneous. If reactions take place upon collision of the reacting particles, these particles would have to move with infinite velocities for a precipitation to be instantaneous. The slowness of diffusion may be shown by dropping a colored substance, such as potassium dichromate, into a beaker of water and noting how slowly the color diffuses through the solution. The particles may have a rapid vibratory motion, but their translational motion (mobilities) through the solution is not great. When we come to think about it, it is surprising that precipitations are as rapid as they are.

After a precipitant is added, the mixture should be thoroughly shaken or stirred, to assist the diffusion process in bringing the reactants into contact with each other. The mixture should also be allowed to stand a while before filtering.

Precipitation with Hydrogen Sulfide.—Precipitation reactions with hydrogen sulfide deserve particular attention for two reasons: (1) The gas is not very soluble in water, and the reaction proceeds slowly. Care must be taken that the precipitation is complete. (2) The gas is poisonous, and large concentrations in the atmosphere are dangerous.

There are two general methods for precipitation by H_2S : (1) the "bubbling" system, and (2) the "pressure" system. The bubbling procedure in its simplest form is represented in Fig. 8. A stream of the gas in the form of bubbles is made to pass through the solution. The efficiency of the method is low. Absorption of the gas takes place at the surface of the bubbles; and, since the gas is absorbed slowly, most of the gas escapes into the atmosphere of the room or the hood. The pressure system is represented in Fig. 9. After the gas is turned on, the

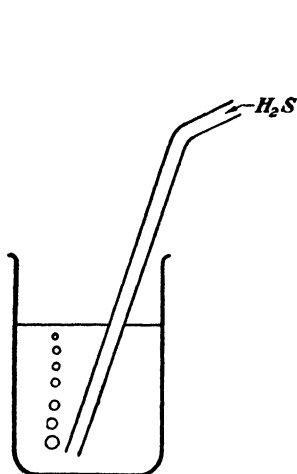


FIG. 8.—The "bubbling" method of precipitation by H_2S .

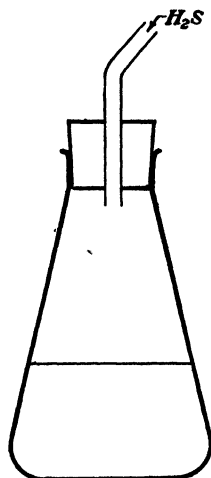


FIG. 9.—The pressure method of precipitation by H_2S .

stopper of the flask is loosened for a moment, so as to displace most of the air in the flask by H_2S . The stopper is then inserted tightly and the flask shaken from time to time. The pressure system has two advantages over the bubbling system, *viz.*: (1) it offers a larger surface to the gas, and (2) it prevents the escape of large amounts of the gas unused. The bubbling system has the advantage that the bubbles keep the solution stirred. The advantages of both systems are combined in the absorption flask illustrated in Fig. 10. Here the gas is allowed to bubble freely until most of the air is displaced from the flask, and then the exit tube is closed by a cock or pinch clamp. As absorption proceeds, gas bubbles through the solution, thereby keeping it

stirred. In any form of the bubbling system, the delivery tube must be cleaned after each precipitation, and care must be taken to keep the solution from "backing up" into the H_2S line.

Digestion.—When conditions permit, the precipitate should be allowed to stand for some time in contact with the "mother liquor" before filtering. There are three principal advantages in this "digestion": (1) The precipitate settles and is not brought on the filter until most of the solution has run through. This saves time. (2) Upon standing, small particles change into large ones, especially if the mixture is heated (*cf.* page 14). Filtering and washing will then

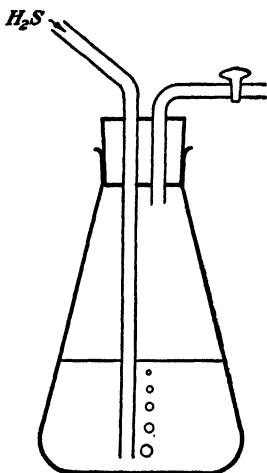


FIG. 10.—Combination of bubbling and pressure methods.

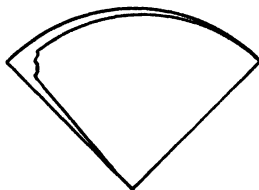


FIG. 11.—Folding filter papers.

proceed more rapidly. (3) Many precipitations require this digestion in order for them to be complete.

Filtration.—This is the most time-consuming operation in qualitative analysis. The process may be hastened in several ways, *viz.*: (1) the conversion of colloidal precipitates into crystalloidal precipitates by digestion and electrolytes, (2) complete precipitation, (3) proper technique in filtration.

Speed in filtration is promoted by making the filter paper, at its upper edges, fit the funnel so closely that air cannot pass between the paper and the glass. If air channels are left, it will not be possible to maintain an unbroken column of filtrate in the stem of the funnel. The weight of this column acts as a mild suction and thereby hastens filtration.

The funnels used in analytical chemistry are supposed to have a 60-deg. angle at the apex. A paper folded in quarters should fit this angle exactly. It is better to "stagger" the

last fold a little so as to make the plane angle slightly more than 90 deg. (Fig. 11). Then the opened paper will fit the funnel only at the upper edges of the paper. This will leave a slight space between most of the paper and the glass, favoring more rapid filtration. Close contact of the paper with the glass impedes filtration. The formation of an air channel along the

fold may be prevented by tearing off the corner of the smaller segment of the filter, as shown in the figure. Occasionally funnels are found where the angle is not exactly 60 deg. A little practice will show how to fold papers so as to secure perfect fits in such funnels.

Spattering should be avoided, not only to prevent loss of materials, but for the sake of cleanliness. Solutions should be

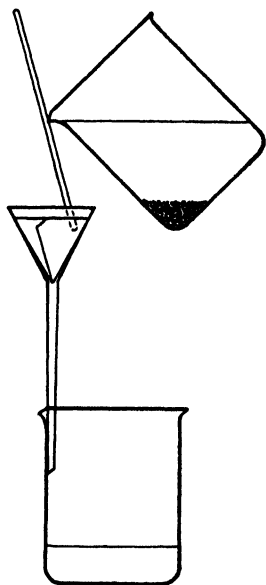


FIG. 12.—Filtration.

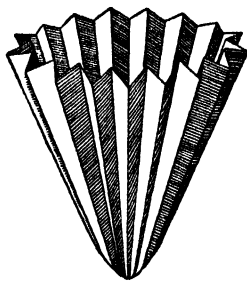


FIG. 13.—Fluted filter paper.

poured on to a filter down a stirring rod, and the stem of the funnel should be in contact with the side of the beaker or dish (see Fig. 12).

Fluted filters (Fig. 13) are sometimes used to hasten filtration. These expose more filtering surface to the solution and also give an increased amount of free space between the paper and the funnel. On the other hand, the suction effect of the filtrate in the stem of the funnel is lost. A similar result is obtained by using a funnel with a "ribbed" surface and folding the paper in the usual way.

Suction Filtration.—Filtration may, in many cases, be hastened by suction, applied by means of a filter flask (Fig. 14) attached

to a filter pump or a vacuum system. The usual arrangement of a filter paper in a 60-deg. funnel cannot be used in a suction system, since the wet paper is not strong enough to support atmospheric pressure and will be ruptured in the apex of the funnel.

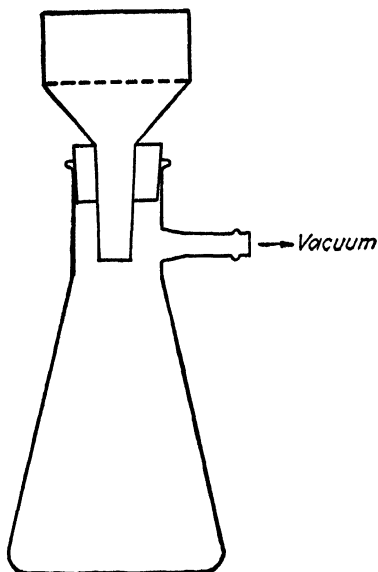


FIG. 14.—Filter flask carrying a Büchner funnel.

This disaster may be avoided by reinforcing the paper at that point with a platinum cone, or a square of cloth may be folded in with the paper to prevent its collapse. Büchner funnels (Fig. 14) furnish a more satisfactory method. These are porcelain funnels with a flat perforated base, over which is placed a filter paper.

There are cases where suction filtration is not successful. Fine colloidal precipitates are drawn into the pores of the paper, plugging them so tightly that filtration proceeds very slowly. Sometimes this colloidal condition may be avoided by better precipitation technique (see page 27). In other cases, this colloidal condition may be unavoidable.

Theory of Washing Precipitates.—Suppose a precipitate already containing 1 cc. of water is washed once with 10 cc. of water. Ten-elevenths of the impurity will be removed, leaving $\frac{1}{11}$, or about 9 per cent. Now, instead of a single washing with 10 cc., suppose that the precipitate is washed twice with 5 cc. After the first washing, $\frac{1}{6}$ of the adsorbed impurity will be left. After the second washing, $\frac{1}{6}$ of $\frac{1}{6}$, or $\frac{1}{36}$, will be left. This is slightly less than 3 per cent. That is, one washing with 10 cc. will remove 91 per cent of the impurity, and two washings with 5 cc. will remove 97 per cent of the impurity. It follows that it is much better (and just about as fast) to wash a precipitate several times with small portions than a few times

with large portions. It may also be seen that each portion should be allowed to drain completely before adding a fresh portion.

This may be expressed algebraically as follows:

Let $x_0, x_1, x_2, \dots x_n$ = weights of adsorbed impurity after successive washings

n = number of washings

a = volume of wash liquid retained by the precipitate

b = volume of wash liquor used each time

Assume that the precipitate already contains a cc. of absorbed water. Then,

$$\text{After first washing, } x_1 = x_0 \cdot \frac{a}{a+b}$$

$$\text{After second washing, } x_2 = x_1 \cdot \frac{a}{a+b} = x_0 \left(\frac{a}{a+b} \right)^2$$

$$\text{After } n \text{ washings, } x_n = x_0 \left(\frac{a}{a+b} \right)^n$$

The theoretical efficiency indicated by this expression is never attained in practice. This is true mainly because washing proceeds too rapidly for the adsorbed impurity to distribute itself uniformly throughout the whole volume of the solution. This is especially true of impurities embedded within the body of the precipitate. Some authorities think that there is a tendency for the impurities in a solution to concentrate themselves on the surface of the precipitate. Such an effect (true adsorption) would further reduce the efficiency of washing.

A precipitate may be washed too much. No precipitate is absolutely insoluble, and some precipitates are only moderately insoluble. Lead chloride is an example of the latter type. If, in the separation of Group I, the precipitate is too thoroughly washed, all the lead chloride may be extracted. No harm is done in this case, because a test for Pb^{++} is always made in Group II. But there are cases when excessive washing of a precipitate might result in the complete loss of an ion. As has been seen before (page 27), some precipitates become colloidal when they are washed too much and tend to run through the filter.

Ignition.—By ignition is meant heating to a high temperature, not inflammation. The flame is applied to the outside of the container, not the inside. For example, a precipitate is ignited to drive off volatile materials or to oxidize or otherwise decompose it. Ignitions are usually carried out in porcelain rather

than glass vessels, since porcelain has a much higher melting point than glass and is usually more resistant to chemical attack.

Use of Test Papers.—Test papers (*e.g.*, litmus) should never be placed in solutions. Rather, a drop of solution should be withdrawn by means of a stirring rod and touched to the paper. If test papers are placed in a solution, the dye will dissolve and may interfere with some of the tests. The paper may disintegrate into a starchy form that will act as a reducing agent toward strong oxidizing agents.

Labeling Solutions.—Confusion and mistakes are sure to result if solutions are not handled in a systematic fashion. Beakers and flasks should be marked by a proper notation on the etched surface provided for the purpose or by means of a “glass” pencil. Test tubes may be labeled by means of pieces of paper placed in their mouths. This is better (and cheaper) than corks, which are apt to become a source of contamination.

Precipitates may be preserved in their funnels by covering them with clean papers or with watch glasses, or they may be transferred along with the paper to properly labeled beakers.

Solutions should be kept covered with watch glasses, not only to protect them from contamination by dust, but to keep down evaporation.

Confirmatory Tests.—After an ion has been separated from other ions, it is customary to apply another test in the form of a reaction that is as specific as possible. This is called a *confirmatory test*. Sometimes the separation form is distinctive enough to make further tests unnecessary, *e.g.*, the black color shown by the residue of Hg_2Cl_2 after the extraction of AgCl by NH_4OH . In many cases, particularly when the ion in question is colorless, there may be little or no evidence of the presence of the ion until a confirmatory test is made. For example, the ammoniacal extract in Group I gives no suggestion of the presence of Ag^+ until it is acidified and AgCl is precipitated.

There are two aspects of confirmatory tests that should be emphasized—specificity and sensitiveness.

Specificity.—Many of the separations of qualitative analysis are not quantitative. As a result, the solution to be tested should contain traces of other ions that have not been completely removed. The confirmatory test should therefore be one not

given by interloping ions but should be wholly characteristic of the ion in question.

Sensitiveness.—A high sensitiveness in confirmatory tests is desirable, so as to test for small amounts. But tests may be too sensitive. For example, the yellow flame test for Na^+ is too sensitive, for it will show Na^+ introduced as an impurity in certain reagents. A less sensitive reagent is more reliable. Really, there is no need that a confirmatory test should be more sensitive than the separations that precede it.

There is sometimes a psychological element in the choice of confirmatory tests. Some people profess that they can see colored precipitates more readily than white ones, and consequently colored reactions are generally given the preference. As an example, Pb^{++} is confirmed as yellow PbCrO_4 instead of white PbSO_4 , though there is little difference in the amounts of the precipitates obtained.

Blank and Control Tests.—In doubtful cases, where the confirmatory test is not all that might be desired, "blank" and "control" tests are helpful. To illustrate: Suppose a very weak test is obtained for Al^{+++} by means of the aluminon reagent. A blank test is made on a solution containing all the reagents leading up to this test, and a control test is made on the same mixture plus a drop of an Al^{+++} solution. The unknown is matched against these known tests.

Evaluation of Sensitiveness.—In order that sensitiveness in tests may have a definite meaning, it is stated in numerical terms. One method is to state the smallest weight of the ion (in grams or milligrams) which, in a volume of 100 cc. of solution, will give a distinct reaction with 1 cc. of the reagent in two or three minutes. For example, 1 cc. of 0.0001 N Mg^{++} diluted to 100 cc. will give a perceptible precipitate with 1 cc. of $\text{Na}_2\text{HPO}_4\text{-NH}_4\text{OH}$ solution after standing 2 min. Now, 1 cc. of 0.0001 N Mg^{++} is 0.00012 g. We therefore report the sensitiveness of this test as 0.00012 g. or 0.12 mg. of Mg^{++} .

Another method of reporting sensitiveness is in terms of the largest volume in which 1 g. of the ion may be detected. For example, the Cl^- test will detect 0.8 mg. of Ag^+ in 100 cc. of solution, or 1 g. in 125,000 cc. The sensitiveness may be briefly expressed as 1 in 125,000:

Exercises

1. Name the processes that may be used in the following separations: (a) gas from liquid; (b) liquid from liquid; (c) solid from liquid.
2. Define *phase*. Name the phases in the following systems: (a) a saturated solution of NaCl; (b) an aqueous solution of NH_3 ; (c) the mixture obtained by grinding together CaO and NH_4Cl .
3. What phases are involved in the extraction of salt from earthy impurities?
4. Carbon dioxide is removed from air by passing the latter through $\text{Ca}(\text{OH})_2$ solution. What phases are involved in the separation?
5. Compare the boiling and melting points of substances that can be sublimed.
6. Name a volatile substance that is separated from solutions with difficulty.
7. Why are precipitates digested in their mother liquor before filtration?
8. Contrast filtration and decantation.
9. Assume that bromine is nine times as soluble in CCl_4 as in water. What would be the theoretical efficiency of extracting bromine solution twice with an equal volume of CCl_4 ?
10. Describe the proper procedure for washing a precipitate, and justify the technique involved.
11. In the latter stages of washing, some precipitates tend to "run through the filter." Explain.
12. Can a precipitate be washed too much? Illustrate.
13. Should a solution in a test tube be shaken against the thumb? Why?
14. Name as many reasons as you can why a "bubbling system" for H_2S should never be used.
15. Can dried precipitates be satisfactorily washed?
16. Calculate the residual impurity (theoretical) when a wet precipitate, weighing 4 g. and containing 0.1 g. of a soluble impurity, is washed five times with 4 cc. of water, 1 cc. being retained by the precipitate at each washing.
17. One cubic centimeter of 0.5 M $\text{Pb}(\text{NO}_3)_2$ diluted to 100 cc. gives a precipitate of PbCl_2 with dilute HCl; upon dilution to 1,000 cc., the precipitate just fails to form. Calculate sensitiveness of the reaction in the usual ways.

CHAPTER V

EQUILIBRIUM AND THE MASS LAW

Occasionally a student misses the point in the discussion of chemical equilibrium, because he thinks of equilibrium as the point at which all action stops, as when a pendulum just ceases to vibrate. Instead of this doctrine of *static* equilibrium, the chemist holds to a doctrine of *dynamic* equilibrium. According to the latter concept, equilibrium consists of reactions that constantly and simultaneously proceed in both directions. The apparent cessation of action is due to the velocities of the reactions becoming equal. A simple illustration is a leaky ship, whose pumps keep the water in the hold at a definite level. The amount of water in the ship thereby remains the same, though it is not the same water at any two successive moments. Briefly stated, equilibrium consists of two opposing reactions, opposite in direction but equal in speed. The resultant effect is therefore zero.

Types of Equilibrium.—It is customary to classify equilibria as (1) physical or (2) chemical. An equilibrium is considered to be physical when the change involved is one of phase and not of composition.¹ To illustrate: The system, ice-water-vapor, consisting of three phases, all of which have the same gross composition, H_2O . A chemical equilibrium, on the other hand, involves the formation of new substances, *e.g.*, $\text{CdS} + 2\text{H}^+ \rightleftharpoons \text{Cd}^{++} + \text{H}_2\text{S}$; or $\text{Bi}^{+++} + \text{Cl}^- + \text{H}_2\text{O} \rightleftharpoons \text{BiOCl} + 2\text{H}^+$. Equilibria are denoted by the double arrow \rightleftharpoons .

¹ The distinction between physical and chemical equilibria is more convenient than real. To illustrate: Water is generally considered a mixture of three substances—monohydrol (H_2O), dihydrol (H_4O_2), and trihydrol (H_6O_3). On the other hand, water vapor consists of monohydrol only. There is then a chemical change when water evaporates. Ice is supposed to be a mixture of higher polymers, as is sometimes indicated by the formula $(\text{H}_2\text{O})_x$. According to this point of view, chemical changes may be involved in all changes of state.

PHYSICAL EQUILIBRIUM

There are several types of equilibrium in which the opposing reactions are physical, or approximately so:

1. Solid \rightleftharpoons melt (fusion).
2. Solid \rightleftharpoons vapor (sublimation).
3. Liquid \rightleftharpoons vapor (evaporation).
4. Solution \rightleftharpoons solution (extraction).
5. Solid, liquid, or gas + solvent \rightleftharpoons solution (solution).
6. Solution \rightleftharpoons solid + solvent (precipitation).

It should be noted that 6 is the reverse of 5, and that 5 and 6 are the most important types of equilibrium to be dealt with in analytical chemistry.

Saturated Solutions.—Saturated solutions furnish a familiar but important example of physical equilibrium. The dynamic

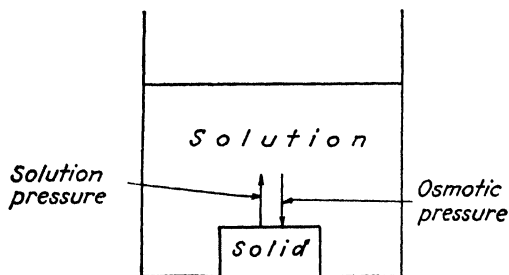


FIG. 15.—Solution and osmotic pressures.

concept has already been given on page 12, where the two opposing reactions were shown to be a tendency for the solid to pass into solution (solution pressure) and a tendency of the solute to reprecipitate (osmotic pressure). In the case of any solid in contact with its saturated solution, the speed of solution is constant, for it is determined by such influences as the temperature, the exposed area of the solid, and so forth. The speed of precipitation is determined by the concentration of the solute in the solution and the area of the solid. Since the area of the solid is the same in both reactions, its effect may be neglected. It follows, then, that the concentration of the solute must be constant in order to maintain a constant speed of precipitation. The condition for a saturated solution (*i.e.*, for a definite temperature) is therefore a definite concentration of solute. This may

be expressed as $[\text{solute}] = K$. This is the simplest case of the mass law.

The Gas-liquid Equilibrium.—In the case of a gas in equilibrium with a liquid, the situation is slightly more complex. The tendency at any given temperature for the gas to escape will be determined by its concentration in the liquid. Calling this escaping tendency \vec{v} , we can say

$$\vec{v} \propto [\text{solute}]_{\text{liquid}} \quad \text{or} \quad \vec{v} = k_1[\text{solute}]_{\text{liquid}}$$

The rate at which the gas will be reabsorbed depends on how frequently gas molecules collide with the surface of the liquid, and that depends upon the concentration of the gas in the gas phase. Calling this solution tendency \overleftarrow{v} , we can say

$$\overleftarrow{v} \propto [\text{solute}]_{\text{gas}} \quad \text{or} \quad \overleftarrow{v} = k_2[\text{solute}]_{\text{gas}}$$

Since at equilibrium $\vec{v} = \overleftarrow{v}$, then

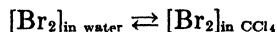
$$k_1[\text{solute}]_{\text{liquid}} = k_2[\text{solute}]_{\text{gas}}$$

or

$$\frac{[\text{Solute}]_{\text{gas}}}{[\text{Solute}]_{\text{liquid}}} = \frac{k_1}{k_2} = K$$

The final constant K is called the *equilibrium constant*.

Solution in Equilibrium with Solution.—This case is exactly analogous to the preceding. An example is the distribution of bromine between two immiscible solvents, such as water and carbon tetrachloride.



The rate at which the bromine will pass from the CCl_4 into the water is determined by its concentration in the CCl_4 , and the rate at which it will pass from the water to the CCl_4 is determined by its concentration in the water. At the equilibrium point, these speeds are equal, and

$$k_1[\text{Br}_2]_{\text{CCl}_4} = k_2[\text{Br}_2]_{\text{H}_2\text{O}}$$

or

$$\frac{[\text{Br}_2]_{\text{CCl}_4}}{[\text{Br}_2]_{\text{H}_2\text{O}}} = \frac{k_2}{k_1} = K_{\text{distribution}}$$

This particular form of the equilibrium constant is called the *distribution* or *partition coefficient*. This distribution between immiscible solvents is the basis of separation by extraction (page 31).

Derivation of the Mass Law.—In the equilibrium, $A + B \rightleftharpoons C + D$, let \vec{v} represent the speed of the forward reaction and \bar{v} the speed of the backward reaction. The forward speed will be determined by the frequency of the collisions between A and B, and that will be determined by how many of these molecules there are per unit volume—*i.e.*, by their concentrations. If we double the concentration of A, we will double the speed of reaction; and if we also triple the concentration of B, we will increase the speed of reaction sixfold. That is, the speed varies as the product (not the sum) of the concentrations of the reactants. This may be represented by the equation

$$\vec{v} = k_1[A][B]$$

In a similar way, the equation for the speed of the backward reaction \bar{v} may be defined as

$$\bar{v} = k_2[C][D]$$

Since at equilibrium these reaction speeds are equal, then

$$k_2[C][D] = k_1[A][B]$$

or

$$\frac{[C][D]}{[A][B]} = \frac{k_1}{k_2} = K_{\text{equilibrium}}$$

This is the algebraic expression of the mass law, and K is called the equilibrium constant.

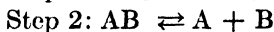
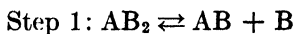
The general usage in setting up a mass law equation is to use the right side of the equation as the numerator of the fraction and the left side as the denominator. Observance of this rule will keep down confusion, for the values of K differ, depending on the procedure.

Stepwise Reactions.—In reactions of the type, $2A + B \rightleftharpoons C + 3D$, the coefficients of each factor become exponents in the mass law expression

$$\frac{[C][D]^3}{[A]^2[B]} = K_{\text{equilibrium}}$$

This follows from the stepwise nature of reactions. As a rule, only two molecules collide at any instant. The chance of a "three-body collision" is very slight. Complex reactions probably consist of a sequence of "bimolecular" reactions, forming intermediate products which, in turn, are used in forming the final products.

To make the issue as simple as possible, let us consider the stepwise dissociation of AB_2 .



The mass law expressions for these steps are

$$\frac{[AB][B]}{[AB_2]} = K_1 \text{ (primary equilibrium constant)}$$

$$\frac{[A][B]}{[AB]} = K_2 \text{ (secondary equilibrium constant)}$$

The concentration of the intermediate product AB may be eliminated by multiplying the expressions together.

$$\frac{[A][B]^2}{[AB_2]} = K_1 \times K_2 = K \text{ ("over-all" equilibrium constant)}$$

It must be insisted that the absence of $[AB]$ from this last expression does not necessarily imply that there is no AB present in the final system. In some cases, it is present in considerable amount; in others, its removal is practically complete. The expression shows only the mathematical relationship existing between the original reactants and the products of the last reaction.

As the dissociation of AB_2 approaches completeness, the concentration of B will approach twice the concentration of A . That is, if the limiting concentration of A is, say 0.02 mole per liter, that of B will be 0.04 mole per liter. So when we substitute in the expression for the "over-all" equilibrium, we have in this case

$$\frac{[A][B]^2}{[AB_2]} = \frac{0.02 \times (0.04)^2}{[AB_2]} = K_{\text{equilibrium}}$$

Sometimes a student has trouble in convincing himself that it is not "overdoing it" both to "double and square" the concentration of the B factor. It should be noted, first, that the concentration of B in the above case is not doubled; it is actually 0.04. That concentration doubled was that of A, and it was doubled in calculating [B]. Second, the squaring is due to the stepwise nature of the reaction, as indicated above. This squaring would be hard to defend if the reaction did not pass through the AB stage. Experimental results justify the use of the square of the B concentration, thereby confirming the assumed existence of AB.

Displacement of Equilibrium.—According to the Le Châtelier principle, if a stress is applied to a system in equilibrium, the equilibrium will be shifted in such a direction as to absorb (or undo) that stress. Many applications are made of this principle in chemical analysis.

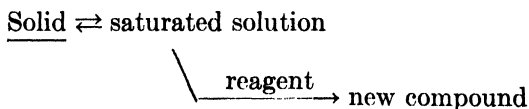
A precipitation is made more complete by using an excess of the precipitant. In the case of $A + B \rightleftharpoons \underline{AB}$, if an excess of B is added, the system will try to absorb this extra B by combining it with A to form more AB. That is, the equilibrium will be shifted to the right.

Heat usually increases the solubility of a material, because the phenomenon of solution is usually endothermic: solute + solvent + heat \rightleftharpoons solution. In rare cases, solution is exothermic. An example: $\text{Na}_2\text{SO}_4 + \text{water} \rightleftharpoons \text{solution} + \text{heat}$. In this latter case, in order to absorb the heat, the equilibrium is shifted to the left, and the salt becomes less soluble (see Fig. 2, page 12).

Suppose a water solution is evaporated. As fast as the water vapor diffuses away from the surface of the solution, the solution forms more vapor in an attempt to maintain its concentration. This process is an illustration of the familiar fact that moisture evaporates more readily in a draft.

Next consider the solution of a compound, slightly soluble in water but readily soluble in some chemical reagent—an acid, for example. The water surrounding this compound may be considered saturated with the compound. The acid reacts with this saturated solution, converting the compound into a new substance of high solubility. The dissolved substance is thus

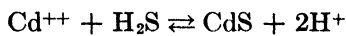
used up, and the solid responds by sending more molecules into solution to maintain a constant degree of concentration, as required by the mass law. The case may be diagrammed thus:



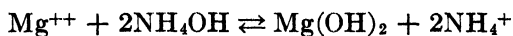
CHEMICAL EQUILIBRIUM

Many of the reactions of analytical chemistry are "reversible," because the products formed in the forward reaction tend to react backward, re-forming the original reactants. The result is an incomplete reaction. Numerous cases may be cited.

1. Cadmium sulfide cannot be completely precipitated by H_2S in strongly acid solution, because it is soluble in moderate concentrations of H^+ ions.



2. Magnesium hydroxide cannot be precipitated completely by NH_4OH , for it is soluble in NH_4^+ ions.



Such incomplete reactions cannot be tolerated in analytical separations, where "clean" separations are necessary for correct results. It is necessary, therefore, to know how to manipulate these incomplete reactions, so as to make them practically complete in one direction or the other.

Homogeneous and Heterogeneous Systems.—There is a second classification of equilibria, as follows: (1) homogeneous systems, in which all the reactants and products are present in one and the same phase, as a solution, or a mixture of gases; (2) heterogeneous systems, in which two or more phases are present, *e.g.*, a saturated solution in contact with an excess of the solid solute, or two solutions of the same solute in immiscible solvents, or a gas in contact with a saturated solution.

Equilibrium Constants.—The mass law holds for all types of equilibria. That is, the products of the proper powers of the concentrations of products and reactants give a definite ratio for definite conditions of temperature, pressure, etc. As stated on

page 45, this ratio is called the equilibrium constant. For gaseous systems, partial pressures may be used instead of concentrations. The numerical values of the constants may not be the same in the two cases, for they are in different units or denominations.

Concentrations of Solids and Pure Liquids.—Concentration has been defined as “moles per liter.” In order to apply this concept to heterogeneous systems, this definition must be extended to solids and liquids. For example, the specific gravity of CaCO_3 is 2.7. A liter of solid CaCO_3 would therefore weigh 2,700 g. Its concentration is then 2,700 g. divided by its molar weight, 100 g.; or $[\text{CaCO}_3] = 27$. Again, 1 l. of water weighs 1,000 g. Its molar weight is 18 g. Therefore its concentration is 1,000 divided by 18, or 55.55. For solids and liquids, the change in volume with change in temperature is very slight—so small that it may be neglected ordinarily. That is, we may consider the concentration of CaCO_3 27, and of water 55.55 for all ordinary temperatures. In other words, their concentrations are constants. And if they are constants, the mass law expressions in which they occur may be simplified by omitting them. For example, consider the equilibrium $\text{CaCO}_3 + \text{heat} \rightleftharpoons \text{CaO} + \text{CO}_2$. The equilibrium constant is

$$K_1 = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]} = \frac{k_1[\text{CO}_2]}{k_2} = k_3[\text{CO}_2]$$

or

$$[\text{CO}_2] = \frac{K_1}{k_3} = K_{\text{equilibrium}}$$

That is, the concentration of the CO_2 in equilibrium with solid CaCO_3 is always the same for a given temperature.

The next point is an important one. The concentration of solid CaCO_3 is not changed by pulverizing it. The density of each particle is the same as in the massive form. When two liquids mix, on the other hand, each dilutes the other, and the concentrations of both are lowered. Suppose we consider the concentration of water in 0.1 molar sugar solution. It is no longer 55.55, but $55.55 - 0.10$, or 55.45. However, this change is so small that it may be neglected. So the concentration of the water in dilute

aqueous solutions may be considered constant without appreciable error.

Homogeneous Systems.—The following types of one-phase systems are to be noted.

Gaseous Systems.—As an illustration, the dissociation of nitrogen dioxide into nitric oxide and oxygen may be cited: $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$. There are two constants for this equilibrium, depending upon whether the "active masses" are expressed in concentrations or partial pressures.

$$\frac{[\text{NO}]^2[\text{O}_2]}{[\text{NO}_2]^2} = K'_{\text{equilibrium}}$$

and

$$\frac{p_{\text{NO}}^2 p_{\text{O}_2}}{p_{\text{NO}_2}^2} = K''_{\text{equilibrium}}$$

K' is not equal to K'' . The first is a ratio of moles per liter; the second, a ratio of pressures.

Another case is the dissociation of NH_4Cl by heat: $\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_3 + \text{HCl}$. Since NH_4Cl is a solid, its concentration may be dropped from the mass law expression. We have then

$$[\text{NH}_3][\text{HCl}] = K'_{\text{equilibrium}}$$

and

$$p_{\text{NH}_3} p_{\text{HCl}} = K''_{\text{equilibrium}}$$

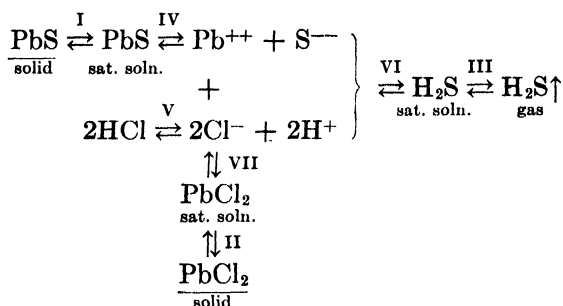
Liquid Systems.—While there are a number of cases of one-liquid systems, the general case has little interest to the analytical chemist, since it is of no use in making separations. The only important form is ionization, which will be considered in a later chapter.

Solid Systems.—These occur in solid solutions (page 9, footnote) and have no applications in analytical chemistry.

Heterogeneous Systems.—Most of the equilibrium systems occurring in analytical chemistry are two-phase systems. Most frequently they consist of a solid in contact with its saturated solution (physical equilibrium) and a homogeneous liquid system of ions and molecules (chemical equilibrium).

An illustration is the solution and precipitation of an insoluble sulfide, such as PbS . PbS is soluble in concentrated HCl ; when

the solution is cooled, a white precipitate of PbCl_2 may form. On the other hand, when the mixture is diluted and saturated with H_2S , black PbS will be reprecipitated. The equilibria involved may be represented as follows:



Equilibria I, II, and III are physical; equilibria IV, V, VI, and VII are chemical.

The mass law can be applied to each of these equilibria singly, as follows:

Equilibrium	System	Mass law expression
I	$\text{PbS}_{\text{solid}} \rightleftharpoons \text{PbS}_{\text{sat. soln.}}$	$[\text{PbS}] = K_{\text{I}}$
II	$\text{PbCl}_{2\text{solid}} \rightleftharpoons \text{PbCl}_{2\text{sat. soln.}}$	$[\text{PbCl}_2] = K_{\text{II}}$
III	$\text{H}_2\text{S}_{\text{gas}} \rightleftharpoons \text{H}_2\text{S}_{\text{sat. soln.}}$	$[\text{H}_2\text{S}] = K_{\text{III}}$
IV	$\text{PbS}_{\text{soln.}} \rightleftharpoons \text{Pb}^{++} + \text{S}^{--}$	$\frac{[\text{Pb}^{++}][\text{S}^{--}]}{[\text{PbS}]} = K_{\text{IV}}$
V	$\text{HCl}_{\text{soln.}} \rightleftharpoons \text{H}^+ + \text{Cl}^-$	$\frac{[\text{H}^+][\text{Cl}^-]}{[\text{HCl}]} = K_{\text{V}}$
VI	$\text{H}_2\text{S}_{\text{soln.}} \rightleftharpoons 2\text{H}^+ + \text{S}^{--}$	$\frac{[\text{H}^+]^2[\text{S}^{--}]}{[\text{H}_2\text{S}]} = K_{\text{VI}}$
VII	$\text{PbCl}_{2\text{soln.}} \rightleftharpoons \text{Pb}^{++} + 2\text{Cl}^-$	$\frac{[\text{Pb}^{++}][\text{Cl}^-]^2}{[\text{PbCl}_2]} = K_{\text{VII}}$

As will be seen later, there are certain inaccuracies in the constants derived by these calculations. For example, HCl does not obey the mass law; some consider HCl completely ionized (page 73); PbCl_2 forms intermediate ions, such as PbCl^+ , which do not appear in the above expressions. Correcting for these

inaccuracies has no effect beyond a slight change in the values of the derived constants.

A number of new and valuable relations may be derived by combining some of the above mass law expressions.

Multiplying	Derived expression	Equilibrium number
I by IV	$[\text{Pb}^{++}][\text{S}^{--}] = K_{\text{VIII}}$	VIII
II by VII	$[\text{Pb}^{++}][\text{Cl}]^2 = K_{\text{IX}}$	IX
III by VI	$[\text{H}^+]^2[\text{S}^{--}] = K_{\text{X}}$	X

Dividing	Derived expression	Equilibrium number
VIII by IX	$[\text{S}^{--}]/[\text{Cl}]^2 = K_{\text{XI}}$	XI
VIII by X	$[\text{Pb}^{++}]/[\text{H}^+]^2 = K_{\text{XII}}$	XII

Another interesting derivation is obtained by multiplying IX by X and dividing the product by VIII.

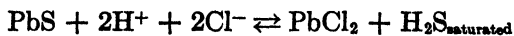
$$\frac{[\text{Pb}^{++}][\text{Cl}]^2 \times [\text{H}^+]^2[\text{S}^{--}]}{[\text{Pb}^{++}][\text{S}^{--}]} = \frac{K_{\text{IX}} \cdot K_{\text{X}}}{K_{\text{VIII}}}$$

Simplifying,

$$[\text{H}^+][\text{Cl}] = \sqrt{\frac{K_{\text{IX}} \cdot K_{\text{X}}}{K_{\text{VIII}}}} = K_{\text{XIII}}$$

This is a rather surprising but true inference; PbS and PbCl_2 can be in equilibrium with each other at only one concentration of HCl . If we attempt to vary this concentration, either PbS or PbCl_2 will dissolve to restore it to this single possible value.

This conclusion might have been reached more simply and more directly. Setting up the over-all equilibrium, by omitting intermediate steps, we have



Now, applying the mass law and dropping out concentrations for solids and saturated solutions, we have

$$[\text{H}^+]^2[\text{Cl}]^2 = K'_{\text{equilibrium}}$$

or

$$[\text{H}^+][\text{Cl}] = K_{\text{equilibrium}}$$

Similar operations may be applied to numerous equilibria occurring in analytical procedures.

False Equilibrium.—Equilibrium is slowly established in some cases. Supersaturated solutions are an example of a metastable system that may persist indefinitely unless precipitation is started in some mechanical way, such as by stirring or by inoculation with a crystal. There are cases where, even in the presence of the solid solute, the mixture must stand for hours or days before true equilibrium is reached.

Supersaturation in solutions of gases is especially hard to break down; prolonged boiling, for example, is necessary to expel SO_2 from a solution. Saturation is also hard to obtain. Prolonged stirring or shaking is necessary to saturate a solution with a solid.

The student is warned that, in the separations of chemical analysis, many cases of false equilibrium will be met and that these cases carry a possibility of error which must not be overlooked.

Exercises

1. Explain why stirring hastens complete precipitation.
2. Explain why a dissolved gas can be removed from a solution more quickly by passing an inert gas through the boiling liquid than by simple ebullition.
3. Suppose that $M \text{ AB}_2$ dissociates stepwise into (1) AB and B and (2) AB into A and B . If the first step proceeds to the extent of 50 per cent and the latter to the extent of 20 per cent, calculate the concentrations of the components of the system.

Ans.: $[\text{AB}_2] = 0.5$, $[\text{AB}] = 0.4$, $[\text{A}] = 0.1$, $[\text{B}] = 0.6$.

4. When 1 mole of $\text{HC}_2\text{H}_3\text{O}_2$ is mixed with 1 mole of $\text{C}_2\text{H}_5\text{OH}$, $\frac{2}{3}$ mole of $\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$ is formed. Neglecting any differences in density, calculate the equilibrium constant.

Ans.: $K = 4$.

5. Solid ammonium chloride dissolves in water with a considerable absorption of heat. Applying the Le Châtelier principle, what sort of solubility curve would you expect?

6. In the equilibrium mixture $\text{N}_2\text{O}_4 + \text{heat} \rightleftharpoons 2\text{NO}_2$, what would be the effect on the color of (1) increasing the pressure on the system, (2) increasing the temperature, (3) diluting with an inert gas at constant pressure?

7. Heat is evolved when anhydrous Na_2SO_4 is dissolved in water. How will its solubility vary with temperature?

8. One mole of NaCl dissolves in 100 moles of water with a slight liberation of heat. The density of the resultant solution is 1.02174, and the density of solid NaCl is 2.18. Show that the result conforms to the Le Châtelier principle.

CHAPTER VI

IONIZATION

The doctrine of ionization was developed in an attempt to explain the conduction of electricity by solutions.

About 1834, Michael Faraday noticed that when a direct current of electricity was passed through a solution, certain constituents moved with the current and others moved against the current. He assumed that the dissolved substance had been decomposed by the current (*electrolysis*) into smaller molecules (*ions*) which carried either positive or negative charges. The ions moving toward the positive pole (*anode*) were assumed to bear negative charges and were called *anions*. The ions moving toward the negative pole (*cathode*) were assumed to carry positive charges and were called *cations*.

Following Faraday, several mechanisms were proposed to explain the orderly manner in which the action proceeded. All these necessitated the assumption that the molecules were bi-part, having what has been called a *plane of cleavage*. Some writers went so far as to assume that molecules undergo momentary decomposition, with the ions "changing partners" as they move toward the electrodes. There were many objections to such theories. In the first place, why should HCl be electrolyzed in water solution and not in nonaqueous solutions like toluene? In the next place, there should be no action until the potential across the cell reaches the value necessary to overcome the electrostatic attraction within the molecule. There is no such critical potential. The least electric stress is sufficient to set up a certain ionic drift. Finally, Hittorf showed that different ions migrate through the solution at different speeds. This cannot be explained by any assumption of disruption of the molecule by means of electrostatic attraction, for that would call for a uniform distribution of cations and anions throughout the solution.

THE THEORY OF PARTIAL IONIZATION

Theory of Arrhenius.—In 1887, the Swedish chemist Svante Arrhenius proposed that solutions which conduct the electric current contain, in addition to the molecules of the solute, some ions produced by their dissociation. For example, a solution of NaCl contains the following: $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$. The dissociation is reversible, as indicated by the double arrow. Apparently Arrhenius considered an ion to be a free atom or radical, carrying one or more electric charges. No hydration of the ions was assumed.

Objections to the Ionic Theory.—The assumption that molecules break down into ions was a shocking proposal to the chemists of 50 years ago. Some of the objections were as follows: (1) The solutions do not show the properties of the free elements. For example, metallic copper is red, and its ion is green; bromine is red, and its ion is colorless; free chlorine is a bleaching agent, and its ion is not. (2) Electrostatic attraction is too strong for molecules to dissociate into charged particles. (3) Molecules are formed from their elements with the evolution of heat. This heat energy must be resupplied for them to dissociate. (4) The free elements cannot be separated by physical means. Iron cannot be removed by a magnet, chlorine by an organic solvent, or a heavy ion by centrifugation. (5) Certain free elements cannot exist in contact with water. Sodium (from NaCl, etc.) should liberate hydrogen and form NaOH.

These objections arose from a misunderstanding of the ionization process, by both its proponents and opponents. Later work has shown that ions do not consist of free elements, as was first thought. For example, the ions in an NaCl solution are not free Na^+ and free Cl^- , but the hydrates of these ions, $(\text{Na} \cdot x\text{H}_2\text{O})^+$ and $(\text{Cl} \cdot y\text{H}_2\text{O})^-$.*

The Hydration of Ions.—The theory that ions are hydrated is confirmed by several lines of evidence: (1) In the first place, solution in general appears to be not a simple dispersion into minute

* In this book, the usual convention of omitting H_2O from the formula of hydrated ions will be followed. This shortening of the formula, though inaccurate, is justified by greater simplicity in equation writing. Furthermore, the number of H_2O molecules in the various ion hydrates is not known.

particles, but a semichemical combination of solute and solvent (solvation). (2) The difference between ions and elements calls for some modification of the latter during the ionization process. (3) But the most important evidence is the transfer of water during electrolysis. Certain substances (*e.g.*, the sugars) are not affected by the passage of an electric current but retain their place in the solution without change in concentration, so that they may be used as reference materials. The water, on the other hand, does not remain fixed in position in the solution but is dragged along with the ions in different amounts. The result is that the solution is diluted at one of the electrodes and concentrated at the other. From this change in the concentration of the water, the relative amounts carried by cation and anion may be calculated. Most authorities assume that the hydrogen ion is a monohydrate, $(\text{H}\cdot\text{H}_2\text{O})^+$ —not H^+ , as Arrhenius proposed—and use it as a reference material. Proceeding on this assumption, the hydration of other ions have been calculated as follows:

H^+	Cl^-	Li^+	Na^+	K^+	Cs^+
1	4	14	8.4	5.4	4.7

Other investigators have studied very dilute solutions and have deduced hydration values much higher than the above.

H^+	OH^-	K^+	Ag^+	Cl^-	NO_3^-	Na^+	SO_4^{--}	Li^+
1	55	110	180	105	125-165	295-355	180	136-318

It has been suggested that the degree of hydration of an ion is not constant but increases with the dilution of the solution.

TABLE 2.—THE PARALLELISM BETWEEN DIELECTRIC CONSTANTS AND THE IONIZING POWER OF SOLVENTS

Liquid	Dielectric constant	Ionizing power
Hydrocyanic acid, HCN	96	Very strong
Water, H_2O	81	Very strong
Formic acid, HCOOH	62	Strong
Methyl alcohol, CH_3OH	33	Moderate
Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$	26	Moderate
Ethyl ether, $(\text{C}_2\text{H}_5)_2\text{O}$	4	Slight
Benzene, C_6H_6	2.3	Trace
Gaseous space.....	1	None

The Ionizing Power of Solvents.—While aqueous solutions of ionogens are good conductors of the electric current, solutions of the same substances in benzene conduct the current very poorly—almost not at all. Why a substance should ionize in one solvent, and not in another, is a hard question. It has been pointed out that the ionizing power of a solvent increases with its dielectric constant (Table 2), which is a measure of its insulating power. This relation, however, is not an exact one, and several exceptions have been noted.

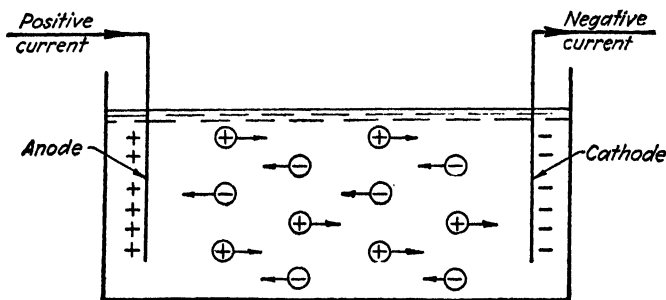


FIG. 16.—Ionic migration during electrolysis.

Evidences in Favor of Ionization.—The ionic theory is supported by the following behaviors of electrolytes:

1. Electric conductivity.
2. Freezing-point depression.
3. Boiling-point elevation.
4. Osmotic pressure.
5. Chemical behavior.

These evidences will be discussed in detail.

1. *Electric Conductivity.*—The motion of the constituents of an electrolytic solution can be explained only by assuming that the moving particles bear electric charges. According to the law of electrostatic attraction and repulsion, like kinds of electricity repel, and unlike kinds attract. As a result, cations, which bear positive charges, are attracted to the negatively charged cathode and are repelled by the positively charged anode; and anions, which bear negative charges, are attracted to the positively charged anode and repelled by the negatively charged cathode. The motion of the ions is shown diagrammatically in Fig. 16.

The ionic theory, it is seen, presumes that dissociation takes place when the ionogen is dissolved. All the electric current does is to sort and discharge the ions. Electrolysis no longer means "decomposition by electricity" in the sense that electricity disrupts the molecule.

The drift of ions in an electrostatic field can be shown by the following experiment.

Cupric chromate, dissolved in a warm 5 per cent solution of agar-agar in water, is placed in the lower part of a U tube (Fig. 17) and is made to set by chilling the mixture. Above the solution in each arm is placed some

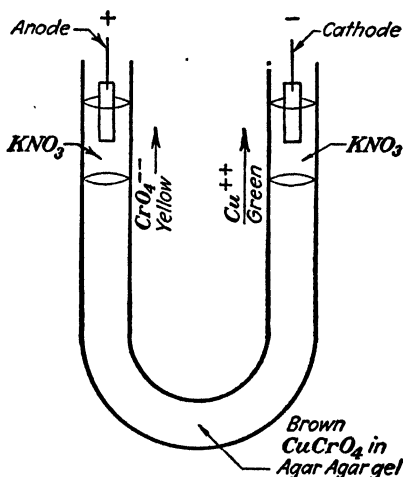


FIG. 17.—Ionic migration in cupric chromate solution.

dilute electrolyte, such as KNO_3 , in which are introduced the electrodes. A current of electricity is passed, care being taken that it is not strong enough to melt the agar-agar jell by its heat effects. Placing the U tube in ice water will help to prevent this. As the electrolysis proceeds, a bluish color will diffuse into the solution around the cathode, and a yellow color into the solution around the anode. This shows that the blue Cu^{++} ions are moving toward the negative pole, and the yellow CrO_4^{--} ions toward the positive pole.

The experiment may be varied to show the migration of colorless ions by introducing into the electrode solutions appropriate materials to serve as indicators. For example, AgNO_3 in the anode region will detect the migration of Cl^- ions, or KCl in the cathode solution will detect Ag^+ ions. $\text{Ba}(\text{NO}_3)_2$ may be used to detect SO_4^{--} , phenolphthalein to detect OH^- , methyl orange to detect H^+ , and so on.

Experiments like these show that the reactions in electrolysis do not take place at the surface of the electrode but occur at a distance.

2. *Freezing-point Depression.*—Molar solutions of nonelectrolytes in water freeze at -1.86°C . We therefore say that the molar freezing point lowering for water is 1.86° . If the freezing points of molar solutions of strong electrolytes are taken, the depressions are much greater. The depression for M KCl is almost $2 \times 1.86^{\circ}$, for M $\text{Ca}(\text{NO}_3)_2$ almost $3 \times 1.86^{\circ}$, and for M $\text{K}_4\text{Fe}(\text{CN})_6$ almost $5 \times 1.86^{\circ}$. This indicates that, upon dissolving, one molecule of KCl breaks down into almost two molecules, one molecule of $\text{Ca}(\text{NO}_3)_2$ into almost three molecules, and one molecule of $\text{K}_4\text{Fe}(\text{CN})_6$ into almost five molecules.

3. *Boiling-point Elevation.*—Molar solutions of nonvolatile nonelectrolytes in water boil at 100.52° under a barometric pressure of 760 mm. That is, the presence of 1 mole per liter of any solute raises the boiling point of water 0.52° . If the boiling points of molar solutions of strong electrolytes are taken, the elevations are much greater. The elevation of M KCl is almost $2 \times 0.52^{\circ}$, of M K_2SO_4 almost $3 \times 0.52^{\circ}$, and of M $\text{K}_4\text{Fe}(\text{CN})_6$ almost $5 \times 0.52^{\circ}$. This indicates that, upon dissolving, these molecules tend to break down into smaller particles—two, three, and five, respectively.

4. *Osmotic Pressure.*—It has been shown on page 17 that the normal osmotic pressure of molar solutions of nonelectrolytes is $22.4 \times T/273$ atm. With strong electrolytes it is much greater—nearly twice this amount for binary electrolytes, nearly three times for ternary electrolytes, and so on. Again we have further independent evidence that electrolytes are dissociated into ions.

5. *Chemical Behavior.*—If AgNO_3 is added to an aqueous solution of HCl, an immediate precipitate of AgCl is obtained. On the other hand, AgNO_3 reacts very slowly with chloroform, CHCl_3 , a precipitate of AgCl appearing only upon standing. The Cl atoms in both cases have a valence of one and seem to be identical in other respects. Prior to the ionic theory, this difference was explained by assuming a difference in stability of the HCl and the CHCl_3 molecules. When a molecule of AgNO_3 collided with a molecule of HCl, the loosely bound Cl

and Ag atoms combined to form the stable AgCl , leaving the H and NO_2 residues to combine with each other. Such a mechanism appeared satisfactory until it was found that the activity of HCl is much less in alcoholic solution and is practically nil in toluene solution. It is not easy to imagine why HCl should be stabilized in such cases, if the solvent is nothing more than an atmosphere.

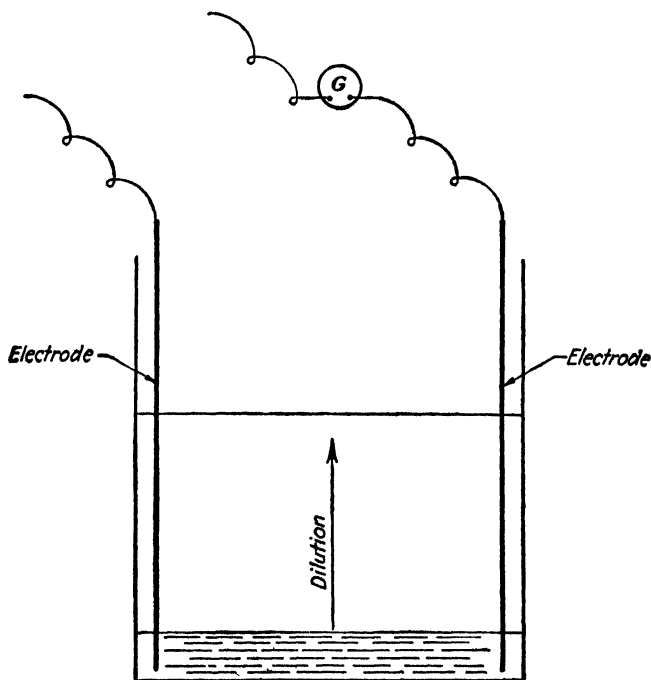


FIG. 18.—Increase of ionization upon dilution.

The ionic theory also explains other aspects of chemical behavior. Ferric hydroxide, $\text{Fe}(\text{OH})_3$, and phosphorous acid, $\text{P}(\text{OH})_3$, have analogous structures. The difference in their behavior is due to the fact that the former acts as a source of OH^- ions, and the latter of H^+ ions.

Again the ionic theory explains why AgNO_3 solution precipitates AgCl from NaCl solution, but none from NaClO_3 or NaClO_4 solutions. As a general rule, ions like ClO_3^- and ClO_4^- are stable and are difficult to break down into the free halogen.

The Degree of Ionization.—The following methods have been used to measure the extent of ionization:

1. *Conductivity Method.*—If a tall, narrow electrolytic cell (Fig. 18), containing a molar solution of a strong electrolyte, is connected with a source of electric current, a certain amount of current will pass, as indicated on the instrument *G*. Now, as water is added to the cell, the amount of current will increase, indicating that more ions have appeared in the solution. The current will continue to increase with dilution, as shown by curve I of Fig. 19, until a concentration of about 0.0001 molar is reached,

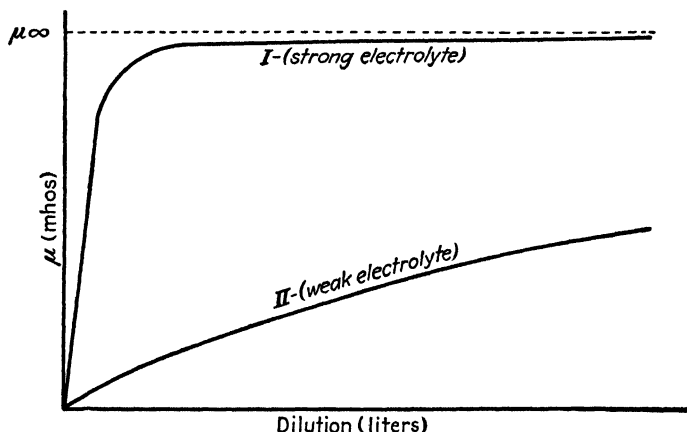


FIG. 19.—Increase in molar conductance with dilution.

when it is practically constant. Ionization may then be assumed to be complete. If ionization may be assumed to be proportional to the amount of current passing, it follows that the fraction ionized at any concentration may be calculated by dividing the conductivity by the maximum conductivity at high dilution.

In practice, an alternating current is used, and what is measured is not the current, but the resistance of a definite volume of solution. The unit of resistance is the *ohm*, and the unit of conductivity is its reciprocal, the *mho*, or the *reciprocal ohm*. The dimensions of the conductivity cell (Fig. 20) are determined by "calibrating" it with some substance of known conductivity, like 0.1 *M* KCl. The conductivity of other solutions in this cell may be obtained by comparison; and from these data may be calculated the conductance of a molar-volume solution, *i.e.*, the

volume of the solution that contains 1 mole. The molar conductivity (molar conductance) is denoted by μ , and the dilution

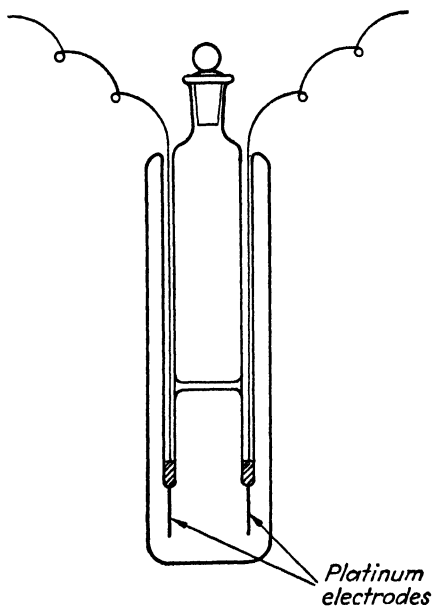


FIG. 20.—Conductivity cell.

indicated by a subscript. For example, the expression for 0.1 *M* KCl is $\mu_{10} = 112$ mhos. μ_{∞} indicates the conductance

TABLE 3.—IONIC CONDUCTANCES AT INFINITE DILUTION

Cations	18°	25°	Anions	18°	25°
H ⁺	314.0	350.0	OH ⁻	172.0	192.0
Na ⁺	43.5	50.9	Cl ⁻	65.5	75.5
K ⁺	64.6	74.5	Br ⁻	67.3	77.4
NH ₄ ⁺	64.5	74.5	I ⁻	66.25	76.1
Ag ⁺	54.3	63.5	NO ₃ ⁻	61.7	70.6
Zn ⁺⁺	91.2	C ₂ H ₃ O ₂ ⁻	34.6	40.8
Pb ⁺⁺	122	SO ₄ ⁻⁻	136.0	158.0
Ba ⁺⁺	110	CO ₃ ⁻⁻	140	

approached by continued dilution, and is read as the molar conductance at infinite dilution.

This method cannot be used to determine the degree of ionization of weak electrolytes directly. Long before the maximum value for μ_{∞} is reached, the conductivity becomes too small to be measured (see curve II in Fig. 19). However, μ_{∞} may be calculated by adding the conductances for the constituent ions (Table 3), which have been determined by other methods. For example, μ_{∞} for $\text{HC}_2\text{H}_3\text{O}_2 = \lambda_{\text{H}^+} + \lambda_{\text{C}_2\text{H}_3\text{O}_2^-} = 312.2 + 33.7 = 345.9$ mhos.

Examples.—1. The molar conductance of 0.1 M AgNO_3 at 18° is 94 mhos. Calculate its percentage ionization, if $\mu_{\infty} = 116$ mhos.

Substituting,

$$\alpha = \frac{\mu_{10}}{\mu_{\infty}} = \frac{94}{116} = 0.8103, \text{ or } 81.03 \%$$

2. Find the percentage ionization of M $\text{HC}_2\text{H}_3\text{O}_2$ at 18° , if its molar conductance is 1.384 mhos. The molar conductance of $\text{HC}_2\text{H}_3\text{O}_2$ for infinite dilution cannot be determined experimentally, but it can be calculated by adding the ionic conductances (Table 3) of the H^+ and $\text{C}_2\text{H}_3\text{O}_2^-$ ions

$$\mu_{\infty} = \lambda_{\text{H}^+} + \lambda_{\text{C}_2\text{H}_3\text{O}_2^-} = 314 + 34.6 = 348.6 \text{ mhos}$$

Hence

$$\alpha = \frac{1.384}{348.6} = 0.004, \text{ or } 0.4 \%$$

2. *E.M.F. Method.*—The concentration of an ion can be determined with great accuracy if it forms what is known as a reversible electrode. For example, the Cu^{++} concentration in a solution may be measured by placing in it a copper rod and determining the potential E assumed by the rod. This value E may be substituted in the Nernst formula

$$E = E_0 + \frac{RT}{nF} \ln [\text{Cu}^{++}] \quad (\text{see page 152})$$

and $[\text{Cu}^{++}]$ calculated from this. The concentration of the other ion of the salt must also be known. The student is referred to textbooks on electrochemistry for detailed discussion. This method is of particular value in determining solubility products.

3. *Freezing-point Method.*—It has been seen (page 60) that a mole of undissociated solute in 1 l. of solution lowers the freezing point of water 1.86° . The number of moles and gram ions present

in any solution may then be determined by dividing the freezing-point lowering by 1.86° .

Examples.—1. A $0.1\ M$ NaCl solution freezes at -0.350° . Calculate the degree of ionization.

The total number of moles and gram ions present is calculated as follows: $0.35/1.86 = 0.188$. In the ionization, $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$, let α = fraction of NaCl ionized. $[\text{Na}^+]$ and $[\text{Cl}^-]$ will each equal $0.1 \times \alpha$, and $[\text{NaCl}]$ will be $0.1(1 - \alpha)$. The total number of moles and gram ions per liter will be

NaCl.....	$0.1(1 - \alpha)$
Na^+	$0.1 \times \alpha$
Cl^-	$0.1 \times \alpha$
<hr/>	
Total.....	$0.1(1 + \alpha)$

Therefore in the case of $0.1\ M$ NaCl

$$\begin{aligned} 0.1(1 + \alpha) &= 0.188 \\ (1 + \alpha) &= 1.88 \\ \alpha &= 0.88, \text{ or } 88\% \end{aligned}$$

2. A $0.18\ M$ $\text{Ca}(\text{NO}_3)_2$ freezes at -0.83° . Calculate its degree of ionization.

The total number of moles and gram ions per liter is $0.83/1.86$, or 0.446 . Assuming that the ionization proceeds according to the equation $\text{Ca}(\text{NO}_3)_2 \rightleftharpoons \text{Ca}^{++} + 2\text{NO}_3^-$, if α = the fractional ionization and the gross concentration is $0.18\ M$, the concentrations will be

$\text{Ca}(\text{NO}_3)_2$	$0.18(1 - \alpha)$
Ca^{++}	$0.18 \times \alpha$
NO_3^-	$0.18 \times 2 \times \alpha$
<hr/>	
Total.....	$0.18(1 + 2\alpha)$

Therefore,

$$\begin{aligned} 0.18(1 + 2\alpha) &= 0.446 \\ 1 + 2\alpha &= 2.48 \\ 2\alpha &= 1.48 \\ \alpha &= 0.74, \text{ or } 74\% \end{aligned}$$

4. *The Boiling-point Method.*—On page 60 it was stated that the presence of a mole of a nonvolatile nonelectrolyte raised the boiling point of a liter of water 0.52° . Therefore the total concentration of molecules and ions in any solution may be calculated by dividing the boiling-point elevation by 0.52 . From this, the fractional ionization α may be calculated.

Example.—A BaCl_2 solution containing 34 g. of solute per liter boils at 100.21° at 760 mm. Calculate the degree of ionization.

Thirty-four grams of BaCl_2 is equivalent to $\frac{34}{208}$, or 0.163 mole. That is, the solution is 0.163 molar. The effective concentration, however, is $0.21^\circ/0.52^\circ$, or 0.404. In the ionization $\text{BaCl}_2 \rightleftharpoons \text{Ba}^{++} + 2\text{Cl}^-$, the concentrations are as follows:

BaCl_2	$0.163(1 - \alpha)$
Ba^{++}	$0.163 \times \alpha$
Cl^-	$0.163 \times 2 \times \alpha$
<hr/>	
Total.....	$0.163(1 + 2\alpha)$

Therefore,

$$0.163(1 + 2\alpha) = 0.404$$

solving,

$$\alpha = 0.74, \text{ or } 74\%$$

5. Osmotic-pressure Method.—It has been seen (page 17) that, for a given temperature, osmotic pressure is determined by the concentration of the solute. If the osmotic pressure of a solution is known, the effective concentration of the solute and its ions can be calculated from the equation $PV = RT$.

Examples.—1. Suppose that a 0.2 M MgSO_4 solution shows an osmotic pressure of 6.272 atm. at 0° . What degree of ionization is indicated?

The effective concentration is 6.272/22.4, or 0.28 M . Since MgSO_4 is a binary electrolyte, for a fractional ionization of α , the total concentration should be

MgSO_4	$0.2(1 - \alpha)$
Mg^{++}	0.2α
SO_4^{--}	0.2α
<hr/>	
Total.....	$0.2(1 + \alpha)$

Solving,

$$0.2(1 + \alpha) = 0.28$$

$$\alpha = 0.4, \text{ or } 40\%$$

2. Calculate the theoretical osmotic pressure of 0.5 M K_2SO_4 (60 per cent ionized) at 27° .

Since K_2SO_4 is a ternary salt, the effective concentration of molecules and ions is $0.5(1 + 2\alpha)$, or, by calculating, 1.10 molar. The osmotic pressure is therefore $22.4 \times 1.1 \times \frac{30}{100} = 27.06$ atm.

This method is of limited usefulness, owing to experimental difficulties. The membrane generally used is $\text{Cu}_2\text{Fe}(\text{CN})_6$, deposited in the walls of porous cells; but even this membrane

tends to develop leaks during a determination, particularly with small particles like electrolytes and their ions.

Comparison of Results by Different Methods.—Table 4 shows some representative results by the conductance and freezing-point methods. The boiling-point and osmotic-pressure methods were not included in the comparison; since, in the first case, temperatures are quite different, and, in the second case, data are neither abundant nor accurate.

With uni-univalent electrolytes, such as KCl and NaNO₃, the agreement is good. But with ternary and bi-bivalent electrolytes, the differences are too great to be explained as experi-

TABLE 4.—IONIZATION VALUES BY DIFFERENT METHODS

Salt	Method	Concentration		
		0.1 <i>M</i>	0.05 <i>M</i>	0.01 <i>M</i>
KCl	Conductance	86.0%	88.9%	94.1%
	Freezing point	86.1	88.5	94.3
NaCl	Conductance	85.2	88.2	93.6
	Freezing point	87.5	89.2	93.8
NaNO ₃	Conductance	83.2	87.1	93.2
	Freezing point	83.0	85.5	90.3
NH ₄ Cl	Conductance			94.1
	Freezing point	85.6	87.8	92.8
BaCl ₂	Conductance	75.9	79.8	88.3
	Freezing point	78.8	81.9	87.8
MgCl ₂	Conductance	76.5	80.3	
	Freezing point	83.9	85.4	88.3
Pb(NO ₃) ₂	Conductance	63.5	70.8	84.5
	Freezing point	64.9	72.4	85.0
MgSO ₄	Conductance	44.9	50.6	66.9
	Freezing point	32.4	42.0	61.8
CuSO ₄	Conductance	39.6	45.5	62.9
	Freezing point		31.8	54.5

TABLE 5.—APPROXIMATE IONIZATION VALUES OF 0.1 MOLAR SOLUTIONS OF STRONG AND WEAK ELECTROLYTES AS 25°

Acids		Bases	
HCl	90 %	KOH	91 %
HNO ₃		NaOH	
HClO ₄		Ba(OH) ₂	77 %
HSCN		NH ₄ OH	1.3 %
H ₂ SO ₄			
H ₃ PO ₄	20-40 %	Salts	
H ₃ AsO ₄		Type of Salt	
H ₂ SO ₃			
H ₂ C ₂ O ₄			
HSO ₄ ⁻			
HNO ₂	5-10 %	C ⁺ A ⁻	
HF		C ⁺⁺ A ₂ ⁻	86 %
		C ₂ ⁺ A ⁻	72 %
		C ⁺⁺ A ⁻	45 %
HC ₂ H ₃ O ₂	1-2 %	KCl	86 %
HC ₂ O ₄ ⁻		NH ₄ Cl	85 %
HSO ₃ ⁻		AgNO ₃	81 %
H ₂ CO ₃	0.1-0.2 %	K ₂ SO ₄	72 %
H ₂ PO ₄ ⁻		Ba(NO ₃) ₂	75 %
H ₂ AsO ₄ ⁻		CuSO ₄	40 %
HCrO ₄ ⁻		MgSO ₄	40 %
HCN	<0.1 %	HgCl ₂	0.01 %
HCO ₃ ⁻		Hg(CN) ₂	< 0.01 %
H ₂ S		HOH	0.1 × 10 ⁻⁵ %
HPO ₄ ⁻			

mental errors. It is not possible to say which results are right and which are wrong. They do agree in indicating approximate degrees of ionization—close enough for the needs of the analyst in his calculations.

Classification of Electrolytes.—It is convenient to classify electrolytes as strong or weak, on the basis of their degree of ionization. Electrolytes ionized above 40 per cent are usually

called *strong*, 5 to 40 per cent *moderately strong*, and below 5 per cent *weak*. Table 5 gives approximate values for the ionization of 0.1 molar solution at 25°. In the cases of dibasic and tribasic acids, the values indicated are for the first H (primary ionization). In a few cases, the ionization values of the acid anions are also given.

Ionization Constants.—The degree of ionization of an electrolyte is usually expressed in terms of the *fraction ionized* and is denoted by the Greek α . V , as in other cases, is the volume containing 1 mole.

Mass law expressions for ionization take various forms, depending upon the type of the electrolyte and the extent of the ionization.

$$\text{CA} \rightleftharpoons \text{C}^+ + \text{A}^- \quad \frac{[\text{C}^+][\text{A}^-]}{[\text{CA}]} = \frac{\frac{\alpha}{V} \cdot \frac{\alpha}{V}}{\frac{1-\alpha}{V}} =$$

$$\frac{\alpha^2}{V(1-\alpha)} = K_{\text{ionization}}$$

$$\text{C}_2\text{A} \rightleftharpoons 2\text{C}^+ + \text{A}^{2-} \quad \frac{[\text{C}^+]^2[\text{A}^{2-}]}{[\text{C}_2\text{A}]} = \frac{\left(\frac{2\alpha}{V}\right)^2 \cdot \frac{\alpha}{V}}{\frac{1-\alpha}{V}} =$$

$$\frac{4\alpha^3}{V^2(1-\alpha)} = K_{\text{ionization}}$$

$$\text{CA}_2 \rightleftharpoons \text{C}^{++} + 2\text{A}^- \quad \frac{[\text{C}^{++}][\text{A}^-]^2}{[\text{CA}_2]} = \frac{\frac{\alpha}{V} \cdot \left(\frac{2\alpha}{V}\right)^2}{\frac{1-\alpha}{V}} =$$

$$\frac{4\alpha^3}{V^2(1-\alpha)} = K_{\text{ionization}}$$

$$\text{CAB} \rightleftharpoons \text{C}^{++} + \text{A}^- + \text{B}^- \quad \frac{[\text{C}^{++}][\text{A}^-][\text{B}^-]}{[\text{CAB}]} = \frac{\frac{\alpha}{V} \cdot \frac{\alpha}{V} \cdot \frac{\alpha}{V}}{\frac{1-\alpha}{V}} =$$

$$\frac{\alpha^3}{V^2(1-\alpha)} = K_{\text{ionization}}$$

It should be noted that the equilibrium constants for ionizations are called *ionization constants* and are designated as " $K_{\text{ionization}}$."

This constant should be carefully distinguished from solubility (or ion) product constants, designated as " $K_{\text{sol. prod.}}$ " (see page 90).

The ionization values for acetic acid in the third column of Table 6 were obtained by the conductance method. From these, the ionization constants in the fourth column were calculated by means of the Ostwald dilution law $K_{\text{ionization}} = \alpha^2/V(1 - \alpha)$. It will be noticed that the constants "check" very closely. Other weak electrolytes obey the mass law equally well. As will be seen later, strong electrolytes do not follow the mass law.

TABLE 6.—IONIZATION CONSTANTS FOR THE WEAK ELECTROLYTE, ACETIC ACID, AT 18°

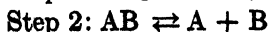
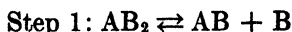
Molarity	$V\left(=\frac{1}{M}\right)$	α (= fraction ionized)	$K = \frac{\alpha^2}{V(1 - \alpha)}$
0.125	8	0.0119	0.0000180
0.0625	16	0.0167	0.0000179
0.03125	32	0.0238	0.0000182
0.015625	64	0.0333	0.0000179
0.007813	128	0.0468	0.0000179
0.003906	256	0.0656	0.0000180

Stepwise Reactions.—The mass law expression for the reaction $2AB_3 + 3C_2D \rightleftharpoons A_2D_3 + 6BC$ takes the form

$$\frac{[A_2D_3] \times [BC]^6}{[AB_3]^2 \times [C_2D]^3} = K_{\text{equilibrium}}$$

It will be noted that the coefficients of the equation become exponents in the mass law expression. This follows from the stepwise nature of reactions.

To make the case as simple as possible, let us consider the dissociation $AB_2 \rightleftharpoons A + 2B$. AB_2 loses only one B at a time, not both B's simultaneously. And in the reverse action, A combines with only one B at a time, and not two at once. The chance of a "three-body collision" is extremely small. The result is, poly-molecular reactions consist of a series of intermediate reactions, each of which may be considered bimolecular. For example:



The mass law expressions for these steps are

$$\frac{[AB] \times [B]}{[AB_2]} = K_1 \text{ (primary equilibrium constant)}$$

$$\frac{[A] \times [B]}{[AB]} = K_2 \text{ (secondary equilibrium constant)}$$

Multiplying these expressions,

$$\frac{[AB] \times [B] \times [A] \times [B]}{[AB_2] \times [AB]} = K_1 K_2$$

Canceling $[AB]$ in numerator and denominator and introducing a new constant for the $K_1 K_2$ term,

$$\frac{[A] \times [B]^2}{[AB_2]} = K \text{ (over-all equilibrium constant)}$$

While this process eliminates the intermediate product AB from the final mathematical expression, it does not eliminate it as a step in the actual mechanism of the dissociation. It remains an essential step in the process and determines the form taken by the final expression.

The next point is equally important. In those cases in which the amount of the intermediate product is small enough to be negligible (*cf.* solubility product, page 91), the concentration of B becomes *twice that of A*; *i.e.*, $[B] = 2[A]$. To put it another way: If x = the fraction of AB_2 dissociated, $[AB_2] = 1 - x$, $[A] = x$, $[B] = 2x$. Note that the concentration of B is *not doubled*; it is *only calculated* in terms of the amount of AB_2 dissociated. The situation may be epitomized as follows: As the system $AB_2 \rightleftharpoons A + 2B$ approaches equilibrium, the stepwise nature of the reaction requires that $[B]$ must be squared, because two steps are involved; and it also requires that $[B]$ must approximate $2[A]$, since $[AB]$ is assumed practically to vanish.

There are cases where the above assumption that $[B]$ approaches $2[A]$ does not hold, *e.g.*, the stepwise dissociation of weak electrolytes. To illustrate: In the ionization of H_2CO_3 , the concentration of CO_3^{--} is not one-half of the H^+ concentration. Really it is only $1/150$ of the H^+ concentration. This follows from the fact that the second step of the ionization of H_2CO_3 is very small in comparison with the first (see page 81).

The Anomaly of Strong Electrolytes.—By this impressive caption is meant that strong electrolytes do not obey the mass law. Table 7 shows the ionization of five concentrations of KCl at 25°, as obtained by the conductance method. When the ionization constants are calculated, it is evident that $K_{\text{ionization}}$ is not constant but increases with the concentration of the electrolyte. This deviation from theory is found in other strong electrolytes, and it is not considered safe to use the mass law in calculating their ionizations.

TABLE 7.—VARIATION OF THE IONIZATION CONSTANT OF POTASSIUM CHLORIDE AT 25°, USING THE CONDUCTANCE METHOD

Concentration	Percentage ionization	Ionization constant
1.0 <i>M</i>	78.5	2.77
0.5 <i>M</i>	78.9	1.475
0.1 <i>M</i>	85.7	0.511
0.05 <i>M</i>	88.8	0.442
0.01 <i>M</i>	93.9	0.145

Defects of the Arrhenius Theory.—The Arrhenius theory of ionization is now under a cloud. Some of the indictments of it are: (1) It does not hold for strong electrolytes; *i.e.*, strong electrolytes do not obey the Ostwald dilution law. (2) Various methods for measuring the degree of ionization do not give concordant results. (3) The principal procedure (the conductance method) for determining the fractional ionization α is known to be inaccurate; *i.e.*, interionic attraction interferes with the migration of the ions, so that conductances vary with the salt content of the solution. (4) The solubility product (page 90) is not strictly constant.

Many efforts have been made to bring these errant ionization data into accord. At first an attempt was made to explain away the irregularities by assuming large degrees of solvation, so that the concentrations at high dilutions are much greater than their calculated values, owing to their using up so much of the solvent in forming hydrates. Corrections for the effect of viscosity in reducing the speed of ions also failed to improve the situation.

THE THEORY OF COMPLETE IONIZATION

Since the beginning of the century there has been a growing dissatisfaction with the Arrhenius theory of partial ionization. This disaffection had its start in the failure of strong electrolytes to obey the Ostwald dilution law. Several writers suggested that strong electrolytes might be completely ionized and that the deviation from ideal behavior might be due to electrostatic attraction between the ions. This new theory has received its strongest support in the fact that some substances appear to be completely ionized in the solid state. For example, X-ray examination indicates that each Cl atom in solid sodium chloride is not combined with any single Na atom, but is spaced equidistant from six Na atoms. The argument is as follows: If there is complete ionization in the solid phase, it should exist all the more in solutions, where the ions are spaced still farther apart. Further, solvation of the ions should help in maintaining this spacing.

The structure of solid NaCl may be grasped by thinking of alternate white and black marbles arranged in layers so that a black marble lies directly above a white marble. A slightly different configuration is found in one form of ammonium chloride. Here each Cl atom is equidistant from eight NH_4 groups. Again the situation may be represented by marbles, only in this case the black marbles lie in the depressions between the white marbles.

The Concept of Complete Ionization.—The complete ionist considers solutions of strong electrolytes to be completely ionized but still retains the concept of incomplete ionization for weak electrolytes. Allowing for electrostatic attraction between the ions, solutions of molarities of 0.001 and less show the behavior of complete ionization very exactly. Solutions of concentrations greater than 0.001 molar do not conform to the new theory much better than to the older Arrhenius theory, and efforts to explain this failure have not been successful.

At high dilutions, except for a certain electrostatic attraction and repulsion, ions are so far apart that they behave independently of one another. At ordinary concentrations, this is not true. Many of the ions approach one another so closely that ion pairs ("doublets") are formed, though the ions do not actually

combine and there is no transfer of electrons. At still greater concentrations, clusters of ions are formed, which may approximate physical units, but without any ion losing its chemical identity. These ion clusters existing in ordinary and concentrated solutions are very complex and presumably do not have any definite composition. No simple law or formula has been proposed that will represent the behavior of any solution except the very dilute ones.

Arguments in Favor of Complete Ionization.—Much evidence may be cited in support of the theory that strong electrolytes are completely ionized:

1. Without doubt, the strongest point in favor of the theory has been the failure of strong electrolytes to obey the mass law.

2. The crystal structure of many substances indicates complete ionization in the solid state.

3. The properties of strong electrolytes appear additive at high dilutions. Certain solutions (*e.g.*, NaCl and KNO₃) may be mixed without any evidence of chemical change. If any NaNO₃ and KCl molecules are formed, there is no heat effect (see page 20) to indicate the chemical change.

4. Partition experiments indicate complete ionization in certain cases. For example: Silver perchlorate, AgClO₄, is readily soluble in benzene, C₆H₆; yet when a solution of AgClO₄ in water is shaken with C₆H₆, no AgClO₄ is extracted, as should be the case if AgClO₄ molecules are present.

5. There is no HCl in the vapor when dilute HCl solution is boiled, indicating the absence of HCl molecules which are volatile.

The Partial Ionist's Rebuttal.—The defects of the original theory of Arrhenius are freely admitted. Ions are no longer considered to be free elements, but hydrates bearing electric charges. But there are certain aspects of the behavior of strong electrolytes that are hard to explain except in terms of molecules.

1. There is no sharp distinction between strong and weak electrolytes, and no one considers the latter completely ionized.

2. If the properties of electrolytes are really additive, the freezing- and boiling-point behaviors of various electrolytes should be parallel.

3. Liquid hydrogen chloride (anhydrous) is not a conductor of electricity. Likewise its solutions in solvents like benzene

are not ionized. If molecules exist in these cases, why not in others?

4. The oxidizing action of certain oxidizing agents (*e.g.*, HNO_3) cannot be attributed to their anions (see page 389).

5. The common and uncommon ion effects (pages 85 and 96) are hard to explain except by assuming the existence of molecules in the solutions.

6. The activity of the H^+ ion in HCl is increased by adding NaCl . How is this possible if it is already 100 per cent ionized?

In short, strong electrolytes do not behave as though they are completely ionized.

The Activity Concept.—In order to retain the usefulness of the applications of the mass law to ionization, Prof. G. N. Lewis of the University of California has proposed what is called the *activity theory*. By definition, the activity of an ion is its concentration multiplied by an appropriate coefficient γ giving an empirical value for the concentration that will bring the behavior of the ion into line with the mass law. To illustrate: The expression for the ionization constant for the salt CA would be

$$\frac{\gamma_1[\text{C}^+] \times \gamma_2[\text{A}^-]}{\gamma_3[\text{CA}]} = K_{\text{equilibrium}}$$

The activity coefficient γ approaches 1 for high dilutions; for ordinary concentrations its values give lower effective concentrations than those obtained by means of the conductance method. These coefficients are not constant, even for the same electrolyte, but vary with concentration and with the presence of other electrolytes.

A number of attempts have been made to calculate γ from thermodynamic data, taking into account interionic attraction,

TABLE 8.—ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE AT 25°, CALCULATED BY DIFFERENT OBSERVERS USING DIFFERENT METHODS

Molarity	Freezing point	Freezing point	E.m.f.	E.m.f.	E.m.f.
1.0	0.634	0.593	0.823	0.605
0.5	0.682	0.638	0.762	0.654
0.1	0.796	0.772	0.745	0.814	0.762

and so forth. These calculations are very involved, and results differ considerably according to the procedure followed. Table 8 shows values for γ obtained by different men using data from freezing-point and e.m.f. measurements. The agreement is no better than in the values for α on the basis of incomplete ionization.

THE PRESENT STATUS OF THE IONIZATION THEORY

At the present time, opinion is divided. Physicists and physical chemists prefer to consider strong electrolytes completely ionized, while many inorganic chemists find the theory of incomplete ionization more satisfactory. So far as the calculations of analytical chemistry are concerned, the question of the degree of ionization presents no difficulties. As will be seen later, these calculations are limited almost wholly to weak electrolytes, which both parties agree are partially ionized and follow the mass law closely. Furthermore, data for the activities of weak electrolytes are not forthcoming, and there is no choice but to use the ionization data of the older theory. So, largely for reasons of expediency, the approach used in this book will be that of incomplete ionization.

Influence of the Ionization Theory on Analytical Chemistry.—

Up to the time of Arrhenius, analytical chemistry was nothing but a collection of empirical procedures, worked out by repeated "cut-and-try" experiments. The laboratory directions were meticulously specific as to such details as volumes used, order of mixing, amount of stirring, and frequently other influences now known to be insignificant. No particular reasons were assigned for these details except that they "gave the right results." Ostwald and his students at Leipzig deserve major credit for the theoretical basis of analytical chemistry as it exists today. Starting with the concept of equilibria between ions and molecules, they were able not only to explain procedures that had previously been wholly empirical but to discover many new methods. In the few decades following the advent of the ionic theory, theoretical analytical chemistry has made as much progress as it had made in the preceding centuries.

Summary.—It may be well to summarize ionization, not as a theory, but as a working hypothesis, as follows:

The molecules of an electrolyte dissociate into ions; these ions later approach one another, re-forming molecules, or at least ion pairs. Equilibrium is reached when the speed of recombination becomes equal to the speed of ionization. Since both of these speeds are determined by the concentrations of the reacting substances, the equilibrium should be expressible by the mass law. A difficulty lies in the uncertainty about the degree of ionization. Dissociation data obtained by the conductivity method are now considered inaccurate unless elaborate corrections are applied. As a result, empirical activities have been proposed as a substitute. However, the activities calculated by different workers do not agree, nor are they available in all cases. Strong electrolytes do not obey the mass law, and the mass law cannot be used in calculations of their concentrations or dissociations. Weak electrolytes obey the mass law well, and it is very useful in calculating their behavior.

Exercises

1. Is anhydrous HCl an electrolyte or an ionogen?
2. Calculate the concentration of the molecules and ions in (a) 0.1 *M* Ba(OH)₂ (80 per cent ionized), (b) 0.2 *M* KAl(SO₄)₂ (40 per cent ionized), (c) 0.2 *M* K₄Fe(CN)₆ (30 per cent ionized). Neglect any stepwise ionization.
3. Ten cubic centimeters of 0.2 *M* NaCl is mixed with 15 cc. of 0.2 *M* HCl. Calculate the concentrations of the Na⁺, H⁺, and Cl⁻ ions, assuming complete ionization of both materials.
4. What is the concentration of the molecules and ions in a solution containing 12 g. of CaBr₂ in a volume of 100 cc.? Assume 80 per cent ionization.
5. A solution contains 2.19 g. of CaCl₂·6H₂O in a volume of 100 cc. Calculate ionic concentrations, assuming an ionization of 90 per cent.
6. How would you account for the Br⁻ ion being colorless and not red?
7. The molar conductance of NaCl is 91.8 mhos for molar solution and 109.3 for infinite solution. Calculate the ionization of *M* NaCl.
8. The molar conductance of CuSO₄ is 87 mhos for 0.1 molar solution, 108 mhos for 0.01 molar solution, and 220 mhos for infinite dilution. Calculate the ionization of 0.1 *M* CuSO₄ and 0.01 *M* CuSO₄.
9. The molar conductance of 0.1 *M* HC₂H₃O₂ is 4.5 mhos. The mobilities of the H⁺ and C₂H₃O₂⁻ ions are 312.2 and 33.7. Calculate the percentage of ionization.
10. The molar conductance of *M* ZnSO₄ is 57.3 mhos. Calculate its ionization from its ionic conductances.
11. Molar NaCl freezes at -3.46°. Calculate ionization.

12. A solution of 6.3 g. of $\text{Hg}(\text{CN})_2$ in 250 cc. of water freezes at -0.186° . Calculate ionization.

13. A solution of 5 g. of sugar in 100 cc. of water freezes at -0.272° . What is its molecular weight?

14. Calculate the boiling point of 0.05 *M* CuSO_4 (40 per cent ionized).

15. 0.356 *M* $\text{K}_4\text{Fe}(\text{CN})_6$ boils at 100.57° and 760 mm. Calculate percentage of ionization.

16. 0.5 *M* NaCl is 75 per cent ionized. Calculate its osmotic pressure at 25° .

17. 0.1 *M* CaCl_2 gives an osmotic pressure of 5.35 atm. at 25° . Calculate ionization.

18. What concentration of urea, $(\text{NH}_2)_2\text{CO}$, in grams per liter, will be required to give an osmotic pressure of 9.77 atm. at 25° ?

19. Calculate the ionization constant for HNO_2 , if 0.04 *M* HNO_2 is 10 per cent ionized.

20. What is the ionization constant of HCN if a 0.1 molar solution is 0.005 per cent ionized?

21. The primary ionization constant for H_2CO_3 is 3×10^{-7} , and the secondary constant is 6×10^{-11} . Calculate the over-all constant *K*.

22. Molar HCl is 78 per cent ionized; 0.1 *M* HCl is 90 per cent ionized. Calculate ionization constants. Does the ionization of HCl conform to the mass law?

CHAPTER VII

APPLICATIONS OF THE IONIC THEORY

In Chap. VI, the status of the ionic theory was stated to be indefinite, owing to differences among chemists as to the mechanism of the ionization process. Consequently any derivations based upon ionic equilibrium might appear to be of doubtful value. Such, however, is not the case. The equilibrium concept, in some form, is necessary in carrying out many of the calculations of chemistry, and the results derived by it fit the experimental facts with surprising accuracy. This chapter deals with certain applications of the mass law to ionic equilibria, which, however insecure their theoretical basis, are essential in the calculations of analytical chemistry.

IONIZATION CONSTANTS

*As seen on pages 69 to 71, ionization constants are derived by substituting in the mass law expression for the equilibrium between molecules and ions. The concentrations of molecules and ions are obtained in two ways: (1) by multiplying the molarity M of the solution by the fractional ionization α ; or (2) (which amounts to the same thing) by dividing α by V , the volume in liters that contains 1 mole.

Example.—0.5 M $\text{HC}_2\text{H}_3\text{O}_2$ is 0.6 per cent ionized. Calculate $K_{\text{ionization}}$.

The equilibrium involved is $\text{HC}_2\text{H}_3\text{O}_2 \rightleftharpoons \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^-$, and the mass law expression is

$$K_{\text{ionization}} = \frac{[\text{H}^+][\text{Ac}^-]^*}{[\text{HAc}]}$$

Here $\alpha = 0.6\%$, or 0.006; $1 - \alpha = 99.4\%$, or 0.994; $M = 0.5$; and $V = 2$. Substituting,

$$K_{\text{ionization}} = \frac{M\alpha \times M\alpha}{M(1 - \alpha)} = \frac{(0.5 \times 0.006)(0.5 \times 0.006)}{0.5 \times 0.994} = 0.000018$$

* Ac is used as an abbreviation for $\text{C}_2\text{H}_3\text{O}_2$.

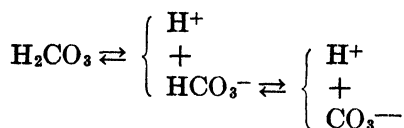
or

$$K_{\text{ionisation}} = \frac{\frac{\alpha/V \times \alpha/V}{1 - \alpha}}{V} = \frac{0.006/2 \times 0.006/2}{0.994/2} = 0.000018$$

Ionization constants are important for the following reasons: (1) They are a measure of the chemical activity of the substance; the smaller the constant, the less the reactivity. (2) They are used in deriving other constants used in calculating solubilities, hydrolysis, and so forth.

Stepwise Ionization of Weak Electrolytes.—A molecule forming a single cation and a single anion is called *binary*. If both ions are univalent, it is said to be uni-univalent (as, for example, NaCl); if both are bivalent, it is bi-bivalent (as, for example, CuSO₄); if both are trivalent, it is tri-trivalent (as, for example, FePO₄). A molecule forming three ions is called *ternary* and may be uni-bivalent, such as K₂SO₄, or bi-univalent, as CaCl₂.

Weak ternary electrolytes ionize in steps. Illustrating by H₂CO₃,



These steps have different ionization constants, denoted by primary (K_1) and secondary (K_2).

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad (\text{primary ionization})$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{--}]}{[\text{HCO}_3^-]} \quad (\text{secondary ionization})$$

This second step proceeds to a much less extent than the first, so that K_2 is smaller than K_1 . As a result, there is always a considerable amount of HCO₃⁻ left in the solution; really the concentration of HCO₃⁻ is more than one million times that of the CO₃⁻⁻ ion. Hence it follows that calculations based on the assumption that H₂CO₃ ionizes directly into 2H⁺ + CO₃⁻⁻ are necessarily erroneous. Another point—since there can be only one value for the concentration of an ion in one and the same solution, the value of [H⁺] in the secondary ionization must be

the same as $[H^+]$ in the primary ionization. These points are brought out in the following problem:

Example.—The values of K_1 and K_2 for H_2CO_3 solution are 3×10^{-7} and 6×10^{-11} , respectively. Calculate the concentrations of each of the ions in 0.03 M H_2CO_3 .

Since H_2CO_3 is a very weak acid, $[H_2CO_3]$ approaches 0.03 M very closely, and this value may be used without appreciable error. Further, since the secondary ionization is very small in comparison with the primary, $[H^+]$ and $[HCO_3^-]$ may be considered equal to each other. Therefore,

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{[H^+]^2}{0.03} = 3 \times 10^{-7}$$

$$[H^+]^2 = 0.09 \times 10^{-7}$$

$$[H^+] = 9.49 \times 10^{-5}, \text{ or } 1 \times 10^{-4}, \text{ nearly}$$

Next, substituting in the expression for the secondary ionization,

$$K_2 = \frac{[H^+][CO_3^{--}]}{[HCO_3^-]} = 6 \times 10^{-11}$$

$$K_2 = \frac{(1 \times 10^{-5})[CO_3^{--}]}{1 \times 10^{-5}} = 6 \times 10^{-11}$$

or

$$[CO_3^{--}] = 6 \times 10^{-11}$$

The final concentrations of the ions are therefore as follows: $[H^+] = 9.43 \times 10^{-5}$, $[HCO_3^-] = 9.43 \times 10^{-5}$, and $[CO_3^{--}] = 6 \times 10^{-11}$. The ratio between the H^+ and CO_3^{--} concentrations in 0.03 M H_2CO_3 is therefore $9.43 \times 10^{-5} : 6 \times 10^{-11}$ or 1,570,000:1. On the contrary, in Na_2CO_3 , the concentration of CO_3^{--} does approximate one-half of the Na^+ concentration (not allowing for hydrolysis). Na_2CO_3 , however, is a strong electrolyte.

Strictly speaking, certain corrections should be applied to the above values, owing to the secondary ionization, $HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$. This will involve a slight increase in the H^+ concentration and a corresponding decrease in the HCO_3^- concentration— 6×10^{-11} gram ion in each case. That is, the final $[H^+] = 9.43 \times 10^{-5} + 6 \times 10^{-11} = 9.430006 \times 10^{-5}$, and the final $[HCO_3^-] = 9.43 \times 10^{-5} - 6 \times 10^{-11} = 9.429994 \times 10^{-5}$. These corrections are very insignificant and are neglected in ordinary calculations.

THE OSTWALD DILUTION LAW

This is a modified form of the expression for the ionization constant and is very useful in calculating (1) the degree of ionization of any required concentration of the electrolyte, and (2) the volume V that will contain a required concentration of a particular ion. Its use is limited to weak electrolytes; strong electrolytes (*cf.* The Anomaly of Strong Electrolytes, page 72) do not obey the mass law.

Derivation.—As pointed out above, the concentrations of the ions of a binary electrolyte can be expressed either as $M\alpha$ or as α/V . In these expressions, M is the molarity of the solution, V is the molar volume,¹ and α is the fraction ionized. Substituting these values in the usual form for the ionization constant of a binary electrolyte CA we have

$$K_{\text{ionisation}} = \frac{[C^+][A^-]}{[CA]} = \frac{M\alpha \times M\alpha}{M(1 - \alpha)} = \frac{M\alpha^2}{1 - \alpha}$$

or

$$K_{\text{ionisation}} = \frac{[C^+][A^-]}{[CA]} = \frac{\alpha/V \times \alpha/V}{\frac{1 - \alpha}{V}} = \frac{\alpha^2}{V(1 - \alpha)}$$

These forms will hereafter be referred to as the *exact* forms of the dilution law.

If the electrolyte is weak, $(1 - \alpha)$ will approach 1, and the expressions will take the simpler forms.

$$K_{\text{ionisation}} = M\alpha^2, \text{ or } \frac{\alpha^2}{V}$$

Solving for α ,

$$\alpha = \sqrt{\frac{K}{M}}, \text{ or } \sqrt{KV}$$

These forms will be referred to as the *approximate* forms of the dilution law.

The forms for ternary electrolytes (*e.g.*, $CA_2 \rightleftharpoons C^{++} + 2A^-$) may be derived by substituting in the mass law expression for the over-all ionization of CA_2 .

$$K_{\text{ionisation}} = \frac{[C^{++}][A^-]^2}{[CA_2]} = \frac{M\alpha \times (2M\alpha)^2}{M(1 - \alpha)} = \frac{4M^2\alpha^3}{1 - \alpha}$$

$$K_{\text{ionisation}} = \frac{[C^{++}][A^-]^2}{[CA_2]} = \frac{\alpha/V \times (2\alpha/V)^2}{\frac{1 - \alpha}{V}} = \frac{4\alpha^3}{V^2(1 - \alpha)}$$

The approximate forms, where $(1 - \alpha)$ approaches 1, are

$$K = 4M^2\alpha^3, \text{ or } \frac{4\alpha^3}{V^2}$$

¹That is, the volume containing 1 mole of the solute. The term is exactly analogous to "gram-molecular volume" (G.M.V.) used in problems on gases.

These forms are of no importance, since the primary ionization of weak electrolytes cannot be neglected. That is, $[A^-]$ cannot be assumed to equal $2[C^{++}]$. In the case of strong electrolytes, the dilution law is not applicable.

The uses of the dilution law are illustrated in the following problems.

Exercises.—1. Calculate the percentage ionization of 0.5 M $HC_2H_3O_2$, if K for $HC_2H_3O_2$ is 1.8×10^{-5} .

A. Solution, using the exact formula:

$$K = \frac{\alpha^2}{V(1-\alpha)} = \frac{\alpha^2}{2(1-\alpha)} = 0.000018$$

$$\alpha^2 = 0.000036 - 0.000036\alpha$$

$$\alpha^2 + 0.000036\alpha = 0.000036$$

$$\alpha^2 + 0.000036\alpha + 0.000018^2 = 0.000036 + 0.00000000324$$

$$\alpha + 0.000018 = \sqrt{0.000036000324} = 0.00600003$$

$$\alpha = 0.006 - 0.000018 = 0.005982, \text{ or } 0.6\% \text{ (nearly)}$$

B. Solution, using approximate formula:

$$\frac{\alpha^2}{V} = \frac{\alpha^2}{2} = 0.000018$$

$$\alpha^2 = 0.000036$$

$$\alpha = 0.006, \text{ or } 0.6\%$$

It should be noted that the gain in accuracy in the exact method is not enough to compensate for the extra work involved.

2. What concentration of $HC_2H_3O_2$ is 1 per cent ionized?

A. Solution, using the exact formula:

$$\frac{\alpha^2 M}{1-\alpha} = \frac{0.0001 \times M}{1-0.01} = 0.000018$$

$$0.0001M = 0.000018 \times 0.99 = 0.00001782$$

$$M = 0.1782, \text{ or } 0.18 \text{ molar (nearly)}$$

B. Solution, using approximate formula:

$$\alpha^2 M = 0.0001 \times M = 0.000018$$

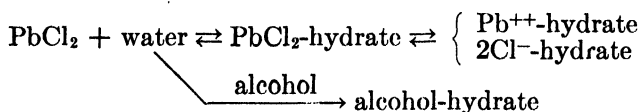
$$M = 0.18 \text{ molar}$$

Again, the increased accuracy of the exact over the approximate method is negligible.

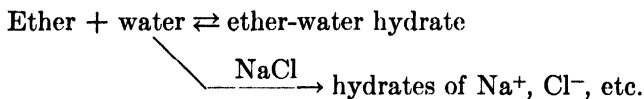
EFFECTS OF OTHER SUBSTANCES ON IONIC EQUILIBRIUMS

According to the original theory of Arrhenius, the presence of other solvents and solutes should have no effect on equilibria. This is now known to be incorrect. In some cases, the effect of adding a second solvent is very conspicuous. The addition of

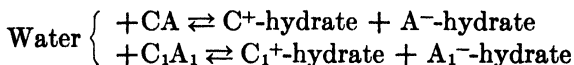
nonelectrolytes reduces the solubility of electrolytes. For example, PbCl_2 is precipitated from a saturated solution by the addition of alcohol. The converse of this case is the separation of one solvent from another by the addition of an electrolyte; *e.g.*, ether is made to separate from water solution by the addition of sodium chloride. This and similar operations are called *salting out*. These actions may be explained by displacement in solvation equilibria. When alcohol is added to saturated PbCl_2 solution, the alcohol combines with the free water to form a solvate, thereby displacing the equilibria leftward.



Ether dissolved in water is present as a solvate. The addition of NaCl withdraws the water to form hydrates of the molecules and ions of NaCl , thereby displacing the equilibrium leftward.



The "Salt Effect."—The effect of a second electrolyte on a solution is more complicated. Assuming incomplete ionization of the type electrolyte CA , it is to be expected that a second electrolyte C_1A_1 would cause a repression of solubility by tying up the solvent water in new hydrates.



Such is now thought to be the case. On the other hand, the solvent for CA is no longer water but C_1A_1 solution. Solutions have higher dielectric constants than water and are for that reason better ionizing mediums (see page 58). As a result, there is double displacement (shown by long arrows) in the equilibria.



This increase in ionization, due to the presence of a second salt, is known as the *salt effect*. For example, the addition of NaCl to

dilute HCl solution causes an increase in the concentration of the H^+ ion. The "incomplete ionist" explains that as an increase in the degree of ionization; the "complete ionist" explains it as an increase in activity.

The Effect of Common Ions on Ionization.—Very fortunately, the calculations of analytical chemistry deal almost wholly with weak electrolytes, which follow the mass law of Arrhenius fairly well.

The ionization of a weak electrolyte may be strongly repressed (*i.e.*, reduced) by adding a strong electrolyte that has an ion in common with the first. To illustrate: The ionization of $HC_2H_3O_2$ is reduced by adding $NaC_2H_3O_2$. Here $C_2H_3O_2^-$ is the "common ion"—*i.e.*, the ion common to the weak and the strong electrolyte.

It may be in place at this time to review the kinetics of ionic equilibrium. In the equilibrium $CA \rightleftharpoons C^+ + A^-$, the speed of formation of CA molecules is determined by the number of collisions per second between C^+ and A^- ions. If the concentration of one of these—*e.g.*, A^- —is doubled, there will be a corresponding increase in the number of CA molecules in the solution. This displacement is offset to some degree by an increase in the speed of dissociation of CA molecules, owing to the increase in their concentration. In the case of the repression of the ionization of the weak electrolyte CA by an excess of the common ion A^- , the situation may be mathematically represented as follows:

Let c = number of C^+ gram ions per liter in pure CA solution; then

c = number of A^- gram ions per liter in pure CA solution.

Let a' = number of gram ions of A^- added, and

x = number of molecules CA formed owing to addition of excess A^- ;

$c - x$ = final concentration of C^+ , and

$c + a' - x$ = final concentration of A^- .

Let m = number of CA molecules per liter in pure CA solution; then

$m + x$ = number of CA molecules per liter after repression.

Substituting in the expression for the ionization constant,

$$\frac{[C^+][A^-]}{[CA]} = \frac{(c - x)(c + a' - x)}{m + x} = K_{\text{ionization}}$$

This expression may be solved for x , giving an exact value for the repression of the ionization, and $(c - x)$ will be an exact value

for the final concentration of C^+ . This approach will be used in the exact method for solving the problem below.

A close approximation to these values may be more easily calculated by assuming that the final concentration of A^- is that of the added electrolyte. To be sure, this would imply that all of the original A^- ions were displaced as CA molecules, thereby removing all the C^+ ions. In other words, ionization would be 100 per cent repressed. This approach is confessedly erroneous, but yet the method gives satisfactory results. This follows from the fact that a' (the increase in $[A^-]$) is so large in comparison with $(c - x)$ that the latter may be disregarded in the expression $(a' + c - x)$. Another approximation is as follows: The concentration of CA molecules approaches the total molarity of CA so closely that the difference is negligible. The simplified expression takes the form

$$\frac{[C^+][A^-]}{[CA]} = \frac{(c - x)a'}{M} = K_{\text{ionisation}}$$

in which M is the molarity of the weak electrolyte. This method will be illustrated in the approximate method below.

Example.—A solution is 0.1 molar in $HC_2H_3O_2$ and 0.5 molar in $NH_4C_2H_3O_2$. Calculate the concentration of H^+ in the mixture assuming that 0.1 M $HC_2H_3O_2$ is 1.3 per cent and 0.5 M $NH_4C_2H_3O_2$ is 80 per cent ionized.

A. Exact method, allowing for the changes in the concentration of the $C_2H_3O_2^-$ ion:

Let x = repression (in moles) of the H^+ and $C_2H_3O_2^-$ ions; then

$$0.0013 - x = \text{final } [H^+];$$

and

$$x = \text{repression of } C_2H_3O_2^-,$$

and

$$0.0013 + 0.4 - x = \text{final } [Ac^-],$$

and

$$0.0987 + x = \text{final } [HAc].$$

Substituting in the expression for the ionization constant of $HC_2H_3O_2$,

$$\frac{[H^+][Ac^-]}{[HAc]} = \frac{(0.0013 - x)(0.0013 + 0.4 - x)}{0.0987 + x} = 0.000018$$

Solving,

$$\begin{aligned} (0.0013 - x)(0.4013 - x) &= 0.0000017766 + 0.000018x \\ 0.00052169 - 0.4026x + x^2 &= 0.0000017766 + 0.000018x \end{aligned}$$

$$x^2 - 0.402618x = -0.0005199134$$

$$x^2 - 0.402618x + 0.201309^2 = 0.040525313481 - 0.0005199134$$

$$x - 0.201309 = \pm 0.2000135$$

$$x = 0.201309 - 0.2000135 = 0.0012955$$

$$0.0013 - x = 0.0013 - 0.0012955 = 0.0000045$$

B. Approximate method, assuming final $[\text{Ac}^-] = 0.4$ and final $[\text{HAc}] = 0.1$:
Substituting in the expression for the ionization constant,

$$\frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} = \frac{[\text{H}^+] \times 0.4}{0.1} = 0.000018$$

$$[\text{H}^+] = 0.0000045$$

It will be noted that the approximate method gives the same result as the longer exact method. This would not be the case if the repressed electrolyte had not been very weak and if an excess of the common ion had not been added.

Common-ion Effect on Strong Electrolytes.—The ionization of strong electrolytes is not strongly affected by the addition of a common ion. This follows from the fact that the increase in the concentration of the common ion is small in comparison with the ions already present, and hence the repression of the other ion is correspondingly small.

Example.—Assuming that strong electrolytes obey the mass law (which is not the case), calculate the concentration of H^+ in a solution 0.1 molar in both HCl and NaCl . Assume that each of these electrolytes is 90 per cent ionized.

The "fictive" expression for the ionization constant of HCl would be

$$\frac{[\text{H}^+][\text{Cl}^-]}{[\text{HCl}]} = \frac{0.09 \times 0.09}{0.01} = 0.81$$

Since we are dealing with strong electrolytes, the final concentrations cannot be approximated. The exact method must therefore be used.

Let x = increase in concentration of HCl molecules due to the common-ion effect

$$\text{Then final } [\text{H}^+] = 0.09 - x$$

$$\text{Final } [\text{Cl}^-] = 0.09 + 0.09 - x = 0.18 - x$$

$$\text{Final } [\text{HCl}] = 0.01 + x$$

Substituting,

$$\frac{[\text{H}^+][\text{Cl}^-]}{[\text{HCl}]} = \frac{(0.09 - x)(0.18 - x)}{0.01 + x} = 0.81$$

Solving,

$$x = 0.0076$$

Therefore, the final $[\text{H}^+]$ is $0.09 - 0.0076$, or 0.0824 molar.

This fanciful problem indicates that the repression of $[H^+]$ is small, only 0.0076 mole. This reduction in acidity is only 8.4 per cent; while in the case of $M HC_2H_3O_2$, cited previously, the reduction was 99.5 per cent.

Buffer Solutions.—As just shown, the ionization of strong electrolytes cannot be repressed to any marked extent by the addition of common ions. However, one of the ions may be repressed by the addition of an ion that will form a weak electrolyte with it. For example, the acidity of an HCl solution may be reduced by adding a salt of a weak acid— $NaC_2H_3O_2$, for example.

Example.—Calculate the final $[H^+]$ if 0.9 mole of solid $NaC_2H_3O_2$ is added to 1 l. of 0.1 M HCl.

One-tenth mole of $NaC_2H_3O_2$ is consumed in converting the 0.1 M HCl into 0.1 M $HC_2H_3O_2$, thus: $H^+ + Cl^- + C_2H_3O_2^- \rightarrow HC_2H_3O_2 + Cl^-$. The remaining 0.8 mole is available to repress the ionization of the 0.1 M $HC_2H_3O_2$ thus formed. Assuming that the 0.8 M $NaC_2H_3O_2$ is 80 per cent ionized, the effective concentration of $C_2H_3O_2^-$ is 0.8×0.8 or 0.64. Substituting in the expression for the ionization of $HC_2H_3O_2$,

$$\frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{[H^+] \times 0.64}{0.1} = 0.000018$$

Solving,

$$[H^+] = \frac{0.000018}{6.4} = 0.000003 \text{ (almost)}$$

In a similar way, the alkalinity of a NaOH solution may be repressed by adding the cation of a weak base. The NH_4^+ ion is the one most commonly used for this purpose.

Example.—How many moles of solid NH_4Cl would have to be added to 100 cc. of M NaOH (85 per cent ionized) to reduce the OH^- concentration to 0.00009?

One hundred cubic centimeters of M NaOH would require 0.1 mole of NH_4Cl to convert it into M NH_4OH : $Na^+ + OH^- + NH_4^+ \rightarrow Na^+ + NH_4OH$. The NH_4^+ concentration required to repress the ionization of M NH_4OH until $[OH^-] = 0.00009$ may be calculated by substituting in the ionization constant for NH_4OH .

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = \frac{[NH_4^+] \times 0.0009}{1} = 0.000018$$

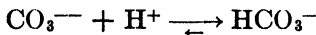
Solving,

$$[NH_4^+] = 0.2 \text{ molar}$$

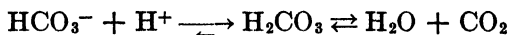
The NH_4^+ content of 100 cc. of 0.2 M NH_4 solution is 0.02 mole. Therefore, the total NH_4^+ required is $0.1 + 0.02$, or 0.12 gram ion. If NH_4Cl of this concentration may be assumed to be 90 per cent ionized, the total NH_4Cl required would be $0.12/0.9$, or 0.133 mole.

This procedure of neutralizing acids and bases by the addition of excess of the salt of a weak electrolyte has a definite advantage over neutralization with bases or acids; *viz.*, the end point cannot be exceeded.

In much the same way, a solution cannot be made acid so long as CO_3^{--} and HCO_3^- ions are present. That is, if an acid is added to a solution containing these ions, the H^+ ions will combine with them, leaving the solution still neutral.



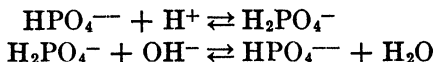
and



The HCO_3^- ion is also a buffer to bases; *i.e.*, it combines with OH^{--} almost completely.



This ion is unique in that it is a buffer to both acids and bases. A mixture of NaH_2PO_4 and Na_2HPO_4 behaves in a similar way. The HPO_4^{--} ion combines with H^+ ions, and the H_2PO_4^- with OH^- ions.



Such solutions are said to have "reserve acidity and alkalinity."

SOLUBILITY PRODUCT

The solubility product is a mass law expression that shows the ionic equilibrium existing in a saturated solution of a slightly soluble electrolyte. It is very important since it is used to calculate (1) the solubility of the substance in electrolytic solutions, and (2) whether a precipitate will form or dissolve when electrolytes are mixed.

Derivation.—The usual method of deriving the solubility product is based upon the stepwise equilibrium



Applying the mass law to the second of these equilibria, we have

$$\frac{[C^+][A^-]}{[CA]} = K_{\text{ionization}}$$

For the time being, we may assume that $[CA]$ is a constant, since we are dealing with a saturated solution. Hence,

$$\frac{[C^+][A^-]}{k} = K_{\text{ionization}}$$

or

$$[C^+][A^-] = k \times K_{\text{ionization}} = K_{\text{sol. prod.}}$$

It is necessary to assume that, in the solution process, the substance ionizes stepwise. Otherwise, the exponential form for ternary electrolytes cannot be justified.

This new constant must be carefully distinguished from the ionization constant. It can be applied only to saturated solutions (heterogeneous equilibria), while the ionization constant is used with homogeneous systems, usually unsaturated. The student should also note the difference in mathematical form—the solubility product expression has no denominator.

The validity of the above derivation of the solubility product in the presence of strong electrolytes is open to question. In the first place, $[CA]$ is not a constant. The solubility of CA is most certainly reduced by the presence of other substances in the solution. In the second place, the ionization of CA is increased by the presence of strong electrolytes (the salt effect, page 84), so that the ionization constant of CA is not constant. However, careful experimental work has shown that solubility products are constants, or very nearly so. The derivation of a truth from two incorrect premises can only be explained on the basis of compensating errors. Possibly the loss in solubility is offset by the increase in ionization, as represented by the long arrows in the following:



The solubility product constant may also be derived by considering the dissolved electrolyte to be completely ionized; *i.e.*, $CA(\text{solid}) \rightleftharpoons C^+ + A^-$. The principle of the derivation is that the

ions in the surface of the solid have different solution pressures, so that unequal amounts of C^+ and A^- are in contact with the solution. For further details, see modern textbooks on physical chemistry.

Complete Ionization of Slightly Soluble Electrolytes.—Slightly soluble precipitates may, in general, be regarded as strong electrolytes whose ionization is interrupted by limited solubility. Since solubility product calculations are limited to concentrations of 0.01 molar and less, complete ionization may be assumed in all cases. This statement also applies to ternary solutes which ionize stepwise. For example, saturated Ag_2CrO_4 is considered completely ionized, forming Ag^+ and CrO_4^{--} ions in the ratio 2:1.

Methods for Calculating Solubility Products.—Values for solubility product constants are obtained in several ways.

1. *Solubility Method.*—If the substance is fairly soluble, its solubility may be determined directly by the evaporation of a solution to dryness and weighing of the residue. Another procedure is to determine one ion in the saturated solution and calculate the solubility of the substance from this datum; *e.g.*, the solubility of Ag_2SO_4 may be obtained by precipitating the Ag^+ ions as $AgCl$, weighing the latter, and calculating from it the weight of the Ag_2SO_4 .

If the solubility of the substance is low enough to assume complete ionization, the solubility product may be calculated directly from the solubility data.

Example.—The solubility of Ag_2SO_4 in water is 2.6×10^{-2} mole per liter. Calculate $K_{sol. prod.}$.

Assuming 100 per cent ionization, the concentrations are

$$[Ag^+] = 5.2 \times 10^{-2}, [SO_4^{--}] = 2.6 \times 10^{-2}$$

Substituting,

$$\begin{aligned} K_{sol. prod.} &= [Ag^+]^2[SO_4^{--}] = (0.052)^2 \times (0.026) \\ &= 7 \times 10^{-5} \end{aligned}$$

There are occasional cases where complete ionization may not be assumed, owing either to considerable solubility or to abnormal ionization. To illustrate:

Example.—The solubility of $PbCl_2$ in water is 0.04 mole per liter. Calculate the solubility product on the assumption of 90 per cent ionization.

The concentrations of Pb^{++} and Cl^- are (0.04×0.9) and (0.08×0.9) , respectively. Substituting,

$$\begin{aligned} K_{\text{sol. prod.}} &= [\text{Pb}^{++}][\text{Cl}^-]^2 = (0.04 \times 0.9)(0.08 \times 0.9)^2 \\ &= 1.87 \times 10^{-4} \end{aligned}$$

2. Conductance Method.—A favorite method for determining the solubility of slightly soluble electrolytes is the measurement of the electrical conductivity of the saturated solution (*cf.* page 62). Electrochemistry gives us the expression $\mu_{\infty} = \kappa V$, where μ_{∞} is the conductance at infinite dilution (obtained by adding the ionic conductances), κ is the specific conductance of the solution, and V is the volume (in cubic centimeters) containing 1 mole. Solving for V and recalling that $M = 1/V$, the concentration is easily obtained. Appropriate assumptions must be made with regard to ionization.

Example.—The specific conductance of saturated AgBrO_3 at 20° is 0.000664 mho. The ionic conductances of Ag^+ and BrO_3^- are 54 and 46 mhos, respectively. Calculate the solubility product. Assuming an ionization of 95 per cent (that of AgNO_3 of corresponding concentration), calculate the total solubility of AgBrO_3 .

Recalling that the conductivity at infinite dilution is the sum of the ionic conductances,

$$\mu_{\infty} = \mu_{\text{Ag}^+} + \mu_{\text{BrO}_3^-} = 54 + 46 = 100 \text{ mhos}$$

Substituting in $\mu_{\infty} = \kappa V$,

$$100 = 0.000664V$$

Solving,

$$V = \frac{100}{0.000664} = 150,602 \text{ cc.} = 150.6 \text{ l.}$$

Since $M = 1/V$, the concentration of the ionized AgBrO_3 is $1/150.6$, or 0.0066 mole per liter. Hence, $[\text{Ag}^+]$ and $[\text{BrO}_3^-]$ each equal 0.0066 M . Upon the assumption of 95 per cent ionization, the total solubility of $\text{AgBrO}_3 = 0.0066/0.95 = 0.007$ mole per liter.

3. E.M.F. Method.—The concentration of most ions may be determined very accurately by means of e.m.f. measurements, *e.g.*, Ag^+ in the presence of an excess of Cl^- of known concentration. From these concentrations, the solubility product may be calculated, and from it the solubility of AgCl in water.

Example.—The concentration of Ag^+ in a saturated solution of AgCl in 0.1 M KCl was found to be 2.24×10^{-9} . Assuming that 0.1 M KCl is

85 per cent ionized, the concentration of the Cl^- ion is 0.1×0.85 , or 0.085. Substituting the expression for the solubility of AgCl ,

$$[\text{Ag}^+][\text{Cl}^-] = (2.24 \times 10^{-9}) \times 0.085 = 1.91 \times 10^{-10}$$

$$\text{Solubility of AgCl} = \sqrt{1.91 \times 10^{-10}} = 1.38 \times 10^{-5}$$

Significance of Solubility Product.—As seen from its derivation, the solubility product states the numerical relation that must exist between the ions of a saturated solution in contact with its precipitate. If this relation is not fulfilled, there can be no equilibrium, and precipitation or solution will take place until the product of the ionic concentrations becomes equal to the solubility product. If the product of the ions exceeds the solubility product, precipitation will occur; if it is less than the solubility product, solution will occur.

The solubility product has then a threefold utility: it may be used (1) to calculate solubilities, (2) to predict when a precipitate may be expected to form, and (3) to predict when a precipitate may be expected to dissolve. These will be illustrated in the following examples.

Examples.—1. Electromotive force measurements indicate that the solubility product of Ag_2S is 1.6×10^{-49} . Calculate its molar solubility.

Let x = molar solubility of Ag_2S

Assuming complete ionization, then

$2x$ = concentration of Ag^+ , and

x = concentration of S^{--}

Substituting in the expression for the solubility product,

$$[\text{Ag}^+]^2[\text{S}^{--}] = (2x)^2 \times x = 1.6 \times 10^{-49}$$

$$4x^3 = 160 \times 10^{-51}$$

$$x^3 = 40 \times 10^{-51}$$

$$x = 3.42 \times 10^{-17}$$

2. Will a precipitate of Ag_2SO_4 form in a solution containing 0.01 M Ag^+ and 0.01 M SO_4^{--} ? The solubility product of Ag_2SO_4 is 7×10^{-5} .

Substituting in the solubility product expression,

$$[\text{Ag}^+]^2[\text{SO}_4^{--}] = 0.01^2 \times 0.01 = 0.000001, \text{ or } 1 \times 10^{-6}$$

This product of the ionic concentrations is less than the solubility product, and no precipitate will form.

3. Calculate the solubility of FeS in M HCl (0.4 per cent ionized). The solubility product of FeS is 3.6×10^{-19} , and that of saturated H_2S (0.1 M) is 1.2×10^{-23} .

The expressions for the solubility products of FeS and H₂S are divided, the first by the second, so as to eliminate [S²⁻].

$$\frac{[\text{Fe}^{++}][\text{S}^{--}]}{[\text{H}^+]^2[\text{S}^{--}]} = \frac{3.6 \times 10^{-19}}{1.2 \times 10^{-22}}$$

$$\frac{[\text{Fe}^{++}]}{[\text{H}^+]^2} = 3 \times 10^4$$

Substituting the value of [H⁺] in *M* HC₂H₃O₂,

$$\frac{[\text{Fe}^{++}]}{0.004^2} = 3 \times 10^4$$

$$[\text{Fe}^{++}] = 3 \times 16 \times 10^{-8} = 0.48$$

The solubility of FeS in *M* HC₂H₃O₂ is therefore 0.48 mole per liter.

Repression of Solubility by Common Ions.—In the equilibrium existing between a slightly soluble electrolyte CA and its saturated solution, the latter may be regarded as completely ionized. The term [CA] then disappears, leaving the simplified expression CA (solid) \rightleftharpoons C⁺ + A⁻. With no CA molecules in the solution to take into account, calculations by means of the solubility product expression become very simple. Since [C⁺][A⁻] = a constant, [C⁺] and [A⁻] must vary inversely with respect to each other. If [A⁻] is doubled, [C⁺] is halved, etc. The repression of either ion results in a corresponding diminution in solubility.

As in the repression of ionization of a weak electrolyte by an excess of a common ion, the calculation of the repression of solubility by a common ion can be made by either (1) an exact method or (2) an approximate method.

The general expression for the exact method takes the following form:

$$(c - x)(c + a' - x) = K_{\text{sol. prod.}}$$

where *c* = concentration of either ion in a saturated aqueous solution, *x* = loss in solubility, and *a'* = concentration of the common ion added.

The approximate method uses the equation

$$(c - x)a' = K_{\text{sol. prod.}}$$

The assumption is that (*c* - *x*) is so small in comparison with *a'* that it may be omitted from the (*c* + *a'* - *x*) of the exact equation without appreciable effect. That is, the *concentration of*

the common ion is set wholly by the added electrolyte. These methods are illustrated in the following examples:

Examples.—1. Calculate the solubility of PbSO_4 in 0.1 M H_2SO_4 (90 per cent ionized). The solubility of PbSO_4 in water is 1.5×10^{-4} mole per liter. The solubility product of PbSO_4 is first calculated.

$$\begin{aligned} K_{\text{sol. prod.}} &= \text{Pb}^{++}\text{SO}_4^{--} = (1.5 \times 10^{-4})(1.5 \times 10^{-4}) \\ &= 2.25 \times 10^{-8} \end{aligned}$$

A. Exact method, allowing for changes in the concentration of the SO_4^{--} ion:

Let x = repression of solubility (moles per liter)

$$\begin{aligned} (1.5 \times 10^{-4}) - x &= \text{final } \text{Pb}^{++} \\ (1.5 \times 10^{-4}) + 0.09 - x &= \text{final } \text{SO}_4^{--} \end{aligned}$$

Substituting,

$$\begin{aligned} [\text{Pb}^{++}][\text{SO}_4^{--}] &= (1.5 \times 10^{-4} - x)(1.5 \times 10^{-4} + 0.09 - x) \\ &= (0.00015 - x)(0.09015 - x) \\ &= 0.0000135225 - 0.0903x + x^2 \end{aligned}$$

Solving,

$$\begin{aligned} x^2 - 0.0903x + 0.04515^2 &= 0.0000000225 \\ x - 0.04515 &= \pm 0.045000249 \\ x = 0.04515 - 0.045000249 &= 0.000149751 \\ \text{Final } [\text{Pb}^{++}] &= 0.00015 - 0.000149751 = 0.000000 \\ &= 0.000000249, \text{ or } 2.49 \times 10^{-7} \end{aligned}$$

B. Approximate method, assuming that final $[\text{SO}_4^{--}]$ is 0.09:
Substituting,

$$\begin{aligned} [\text{Pb}^{++}][\text{SO}_4^{--}] &= [\text{Pb}^{++}] \times 0.09 = 0.0000000225 \\ [\text{Pb}^{++}] &= 0.00000025, \text{ or } 2.5 \times 10^{-7} \end{aligned}$$

2. Calculate the solubility of Ag_2SO_4 in 0.5 M AgNO_3 (80 per cent ionized). The solubility product of Ag_2SO_4 is 6.25×10^{-5} .

Substituting in the expression for the solubility product, using the approximate method,

$$\begin{aligned} [\text{Ag}^+]^2[\text{SO}_4^{--}] &= 0.0000625 \\ (0.5 \times 0.8)^2[\text{SO}_4^{--}] &= 0.0000625 \\ [\text{SO}_4^{--}] &= \frac{0.0000625}{0.16} = 0.00039 \end{aligned}$$

3. Calculate the solubility of Ag_2SO_4 in 0.5 M H_2SO_4 (80 per cent ionized).
Substituting in the expression for the solubility product, using the approximate method,

$$\begin{aligned}
 [\text{Ag}^+]^2[\text{SO}_4^{--}] &= 0.0000625 \\
 [\text{Ag}^+]^2(0.5 \times 0.8) &= 0.0000625 \\
 [\text{Ag}^+]^2 &= \frac{0.0000625}{0.4} = 0.00015625 \\
 [\text{Ag}^+] &= 0.0125
 \end{aligned}$$

Since there are two Ag^+ ions for every molecule of Ag_2SO_4 dissolved, the total solubility of Ag_2SO_4 is $0.0125/2$, or 0.00625 molar.

Increase in Solubility by Uncommon Ions.—It is a well-known fact that the solubility of many salts is increased by the presence of other electrolytes. In many cases, the solvent action is so great that the uncommon ions must be removed before a satisfactory precipitation of the insoluble substance can be made. For example, $\text{Mg}(\text{OH})_2$ cannot be precipitated in the presence of NH_4^+ , or SnS_2 in the presence of $\text{H}_2\text{C}_2\text{O}_4$.

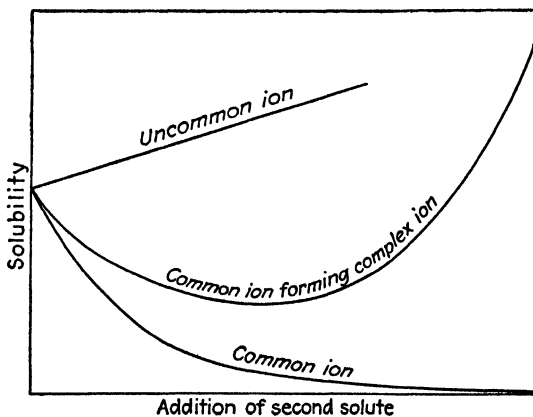
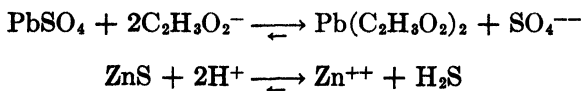


FIG. 21.—Effect of a second electrolyte on solubility.

Usually this increase in solubility is explained by the withdrawal of one or both of the ions of the precipitate to form compounds of low ionization; *e.g.*,



In cases where the possible products are highly ionized, the explanation is not so easy. To illustrate: The solubility of PbSO_4 is appreciably increased by strong electrolytes, such as HNO_3 . The classical explanation is that small concentrations

of molecular $\text{Pb}(\text{NO}_3)_2$ and H_2SO_4 are formed, "making room" in the solution for further dissolving of PbSO_4 . The adherents of the theory of incomplete ionization of strong electrolytes insist that no line of demarcation can be drawn between the effects of $\text{C}_2\text{H}_3\text{O}_2^-$ and NO_3^- ; the difference is one of degree only. On the other hand, the complete ionists explain the increase in solubility as a special case of the salt effect (page 84).

Since strong electrolytes are involved, the mass law cannot be used in calculating the extent of this "uncommon-ion effect."

Exercises

1. Calculate the ionization constant of phenol, $\text{C}_6\text{H}_5\text{OH}$, (carbolic acid), if the H^+ concentration in a 0.1 molar solution is 4×10^{-7} .

Ans.: 1.6×10^{-12} .

2. Calculate the primary ionization constant of arsenious acid, H_3AsO_3 , if a 0.01 molar solution is 0.025 per cent ionized. *Ans.*: 6.25×10^{-10} .

3. The primary and secondary ionization constants of sulfurous acid, H_2SO_3 , have been reported to be 1.7×10^{-2} and 5×10^{-6} , respectively. Calculate the over-all ionization constant for $\text{H}_2\text{SO}_3 \rightleftharpoons 2\text{H}^+ + \text{SO}_3^{--}$.

Ans.: 8.5×10^{-8} .

4. May it be assumed from the preceding problem that in a H_2SO_3 solution the concentration of the H^+ ion is double that of the SO_3^{--} ion? Explain your answer.

5. Calculate the concentration of the H^+ ion in saturated H_2S (0.1 *M*), if K_1 is 0.91×10^{-7} .

6. From the result in the preceding exercise, calculate the concentration of the S^{--} ion in saturated H_2S , if K_2 is 1.2×10^{-15} . *Ans.*: 1.2×10^{-15} .

7. Why cannot the S^{--} concentration in saturated H_2S solution be calculated directly from $K_3 = 1.1 \times 10^{-22}$, assuming that the S^{--} concentration is one-half of the H^+ concentration?

8. The primary and secondary ionization constants of H_2CO_3 are 3×10^{-7} and 7×10^{-11} , respectively. Calculate the H^+ concentration in 0.05 *M* H_2CO_3 .

9. The molar volume of a solution is the volume in liters that contains 1 mole of the solute. Calculate the molar volume of (a) a 0.2 molar solution, (b) a 0.8 molar solution, (c) a 1.25 molar solution. *Ans.*: 5 l., 1.25 l., 0.8 l.

10. Calculate the percentage ionization of 0.25 *M* NH_4OH , if K for NH_4OH is 1.6×10^{-5} . *Ans.*: 0.8 per cent.

11. Calculate the percentage ionization of 0.5 *M* $\text{HC}_2\text{H}_3\text{O}_2$, if K for $\text{HC}_2\text{H}_3\text{O}_2$ is 1.8×10^{-5} . *Ans.*: 0.6 per cent.

12. Molar NH_4OH is 0.4 per cent ionized. Use the Ostwald dilution law to calculate (a) its ionization constant K and (b) the percentage ionization of 0.01 *M* NH_4OH . *Ans.*: 1.6×10^{-5} and 4 per cent.

13. At what concentration is NH_4OH 1 per cent ionized, assuming that its ionization constant is 1.6×10^{-5} ? *Ans.*: 0.16 molar.

14. To what volume must 1 l. of M $\text{HC}_2\text{H}_3\text{O}_2$ be diluted to give a solution 0.003 molar in H^+ ? The ionization constant is 1.8×10^{-5} . *Ans.*: .5 l.

15. Can the Ostwald dilution law be used in calculating dilutions of HCl that will give definite H^+ concentrations? Why?

16. The ionization constant of benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, is 6.48×10^{-5} . Use the Ostwald dilution law to calculate the ionization of 0.2 M $\text{C}_6\text{H}_5\text{COOH}$.
Ans.: 1.8 per cent.

17. The ionization of 0.1 M KOH is 91 per cent. Does this agree with the value calculated by the Ostwald dilution law from the 77 per cent ionization of M KOH ? Why?

18. Calculate the H^+ concentration in a solution that is 0.1 molar in $\text{HC}_2\text{H}_3\text{O}_2$ and 0.5 molar in $\text{NaC}_2\text{H}_3\text{O}_2$ (80 per cent ionized). K for $\text{HC}_2\text{H}_3\text{O}_2$ is 1.8×10^{-5} .
Ans.: 4.5×10^{-6} .

19. What must be the concentration of NH_4^+ in M NH_4OH to reduce the OH^- concentration to 1×10^{-4} ? How can this NH_4^+ concentration be realized? K for NH_4OH is 1.6×10^{-5} .

Ans.: 0.16 molar. By adding 8.56 g. of solid NH_4Cl per liter.

20. Starting with 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$, how would you prepare a solution whose H^+ concentration is 0.0009 molar?

21. Calculate the concentration of S^{--} in a saturated H_2S solution that is 0.25 molar in HCl (100 per cent ionized). The ion product of saturated H_2S is 1.1×10^{-23} .
Ans.: 1.76×10^{-22} .

22. Can a H_2SO_4 solution be buffered by adding solid $(\text{NH}_4)_2\text{SO}_4$? Explain your answer.

23. Five cubic centimeters of 10 per cent $\text{NaC}_2\text{H}_3\text{O}_2$ is added to 5 cc. of 0.01 M $\text{HC}_2\text{H}_3\text{O}_2$. Calculate the final H^+ concentration, assuming the complete ionization of strong electrolytes.

24. One volume of 0.1 M HCl is mixed with 9 volumes of 0.1222 M $\text{NaC}_2\text{H}_3\text{O}_2$ (100 per cent ionized). Calculate the H^+ concentration of the mixture.

25. One-half mole of solid NH_4Cl is added to 1 l. of 0.1 M NaOH . Calculate the OH^- concentration in the mixture, considering all strong electrolytes to be 100 per cent ionized.

26. Calculate the H^+ concentration in the solution obtained by dissolving 10 g. of CaCO_3 in 50 cc. of 6 M $\text{HC}_2\text{H}_3\text{O}_2$ and diluting the mixture to 100 cc. Assume $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ to be 100 per cent ionized. *Ans.*: 9×10^{-6} .

27. Define *buffer*. What is the principle of buffering acidic and basic solutions? Illustrate.

28. Calculate the OH^- concentration in 0.1 M NH_4OH solutions containing the following concentrations of NH_4^+ : (a) 0.01 molar, (b) 0.04 molar, (c) 0.16 molar, (d) 0.64 molar, (e) 1.28 molar. *Ans.*: 0.00016 molar, etc.

29. Name two anions besides $\text{C}_2\text{H}_3\text{O}_2^-$ that may be used to buffer acidic solutions.

30. Why are NH_4^+ salts so generally used to buffer alkaline solutions?

31. Show by equations how the HCO_3^- ion may be used to buffer both acidic and basic solutions.

32. Name some insoluble carbonates that might be used to buffer acidic solutions.

33. What is the effect of precipitating the anions of weak acids from an acidic solution? For example, AgNO_3 is added to Na_2HPO_4 solution.

34. The solubility of MgNH_4PO_4 is 6.3×10^{-8} mole per liter. Calculate its solubility product. *Ans.: 2.5×10^{-13} .*

35. The solubility of $\text{Pb}_2(\text{PO}_4)_3$ is 1.7×10^{-7} mole per liter. Calculate its solubility product.

36. The solubility of PbCrO_4 is 4.3×10^{-5} g. per liter. Calculate its solubility product. *Ans.: 1.77×10^{-14} .*

37. The solubility of Ag_3PO_4 is 6.5×10^{-3} g. per liter. Calculate its solubility product. *Ans.: 1.57×10^{-18} .*

38. The solubility of BaF_2 is 1.25 g. per liter. Calculate its solubility product, assuming 95 per cent ionization.

39. The solubility product of AgCl is 1.21×10^{-10} . Calculate its solubility in (a) moles and (b) grams per liter.

Ans.: (a) 1.1×10^{-5} mole and (b) 1.58 mg.

40. The solubility product of CaF_2 is 3.2×10^{-11} . Calculate its molar solubility. *Ans.: 2×10^{-4} .*

41. If 6.125 g. of KClO_3 dissolve in 100 cc. of water at 25° , what is its molar solubility? Calculate (a) its solubility product and (b) its ionization constant on the assumption of 95 per cent ionization.

42. Criticize the application of the mass law to the calculations of the equilibrium constants of KClO_3 in the preceding problem.

43. The solubility product of Ag_2SO_4 is 6.25×10^{-5} . Calculate its solubility in water.

44. If the solubility product of $\text{Mg}(\text{OH})_2$ were 8×10^{-12} , what would be the solubility of $\text{Mg}(\text{OH})_2$ in water?

45. Sometimes students speak of "doubling" the concentration of the A^- ion when setting up solubility product expressions for precipitates of the type CA_2 . State accurately what is doubled— α , $[\text{C}^{++}]$, or $[\text{A}^-]$.

46. Calculate the concentration of Ag^+ in (a) saturated Ag_2CrO_4 and (b) 0.1 M AgNO_3 (90 per cent ionized) saturated with Ag_2CrO_4 . The solubility of Ag_2CrO_4 is 7.5×10^{-5} .

47. Calculate the solubility of AgCl in 0.2 M HCl (100 per cent ionized). The solubility product of AgCl is 1.2×10^{-10} .

48. Calculate the solubility of SrCrO_4 (100 per cent ionized) in 0.2 M K_2CrO_4 (80 per cent ionized). The solubility of SrCrO_4 in water is 1.2216 g. per liter. *Ans.: 4.58×10^{-2} g.*

49. The solubility product of PbI_2 is 1.4×10^{-8} . Calculate its solubility in (a) 0.1 M CaI_2 (100 per cent ionized) and (b) 1.4 M $\text{Pb}(\text{NO}_3)_2$ (64 per cent ionized). *Ans.: (a) 3.5×10^{-7} and (b) 6.25×10^{-5} .*

50. Calculate the solubility of PbCl_2 in 0.5 M HCl (85 per cent ionized). The solubility product of PbCl_2 is 2.4×10^{-4} .

51. What concentration of H^+ will prevent H_2S from precipitating CdS from a solution containing 0.0009 M Cd^{++} ? Assume the solubility products are as follows: CdS , 3.6×10^{-29} , H_2S , 1×10^{-23} . *Ans.: 5 molar.*

52. What concentration of H^+ will prevent the precipitation by H_2S of PbS in a solution that is 0.0004 molar in Pb^{++} ? The solubility product of PbS is 4×10^{-28} .

53. Calculate the solubility of AgOH in $0.5\text{ }M\text{ NH}_4^+$. The solubility product of AgOH is 2×10^{-8} , and the ionization constant of NH_4OH is 1.6×10^{-5} . (Hint: Write the equation, and note that the concentration of NH_4OH formed is the same as that of the Ag^+ ion.)

Ans.: 2.5×10^{-3} molar.

54. Will a precipitate form if a solution 0.01 molar in Pb^{++} is made 0.02 molar in Cl^- ? The solubility product of PbCl_2 is 2.4×10^{-4} .

55. Should a precipitate form in a solution containing $0.05\text{ }M\text{ Sr}^{++}$ and $0.006\text{ }M\text{ CrO}_4^{--}$, if the solubility product of SrCrO_4 is 3.6×10^{-14} ?

56. How many moles of CaSO_4 would be precipitated if 100 cc. of $0.2\text{ }M\text{ Ca}^{++}$ were mixed with 25 cc. of $0.8\text{ }M\text{ H}_2\text{SO}_4$? Assume all dissolved compounds to be completely ionized. The solubility product of CaSO_4 is 6×10^{-5} .

Ans.: 0.019625 mole.

57. Solutions are mixed so as to give a solution $0.01\text{ }M$ in Mg^{++} , $0.1\text{ }M$ in NH_4OH and $0.02\text{ }M$ in NH_4^+ . Would a precipitate of $\text{Mg}(\text{OH})_2$ form? Its solubility product is 3.4×10^{-11} .

58. Would a precipitate form if equal volumes of $0.04\text{ }M\text{ Ag}^+$ and $0.08\text{ }M\text{ SO}_4^{--}$ were mixed? The solubility product of Ag_2SO_4 is 6.25×10^{-5} .

59. What concentration of SO_4^{--} would be necessary to reduce the solubility of CaSO_4 to $0.003\text{ }M$? The solubility product of CaSO_4 is 2.4×10^{-4} .

Ans.: 0.08 molar.

60. Five hundred cubic centimeters each of $0.2\text{ }M\text{ Ca}^{++}$ and $1.0\text{ }M\text{ SO}_4^{--}$ are mixed. How many moles of CaSO_4 will be precipitated?

Ans.: 0.0994 mole.

61. A solution, 0.09 molar in Mg^{++} and 0.2 molar in NH_4OH , should contain what concentration of NH_4^+ to prevent the precipitation of $\text{Mg}(\text{OH})_2$? The solubility product of $\text{Mg}(\text{OH})_2$ is taken to be 3.6×10^{-11} .

Ans.: 0.16 molar.

62. Calculate the solubility of $\text{Mg}(\text{OH})_2$ in a solution molar in NH_4OH and in NH_4^+ . The ionization constant of NH_4OH is 1.6×10^{-5} , and the solubility product of $\text{Mg}(\text{OH})_2$ is 3.4×10^{-11} .

63. The solubility of Ag_2SO_4 in water is $0.025\text{ mole per liter}$. Calculate its solubility product. Calculate the solubility of Ag_2SO_4 in (a) $0.5\text{ }M\text{ AgNO}_3$ (80 per cent ionized) and (b) $0.5\text{ }M\text{ H}_2\text{SO}_4$ (80 per cent ionized).

Ans.: $6.25 \times 10^{-5}\text{ }M$, $3.9 \times 10^{-4}\text{ }M$ and $6.25 \times 10^{-3}\text{ }M$.

64. Calculate the solubility of CaSO_4 (100 per cent ionized) in $0.1\text{ }M\text{ (NH}_4)_2\text{SO}_4$ (80 per cent ionized). The solubility of CaSO_4 in water is $0.015\text{ mole per liter}$.

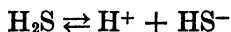
65. Prove by algebra the OH^- concentration of a mixture of a moles of NH_4OH and b moles of NH_4Cl (100 per cent ionized) is independent of the dilution.

CHAPTER VIII

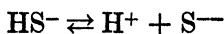
THE PRECIPITATION AND SOLUTION OF SULFIDES

Hydrogen sulfide is the fundamental reagent in the separation of the cation groups. It is used to precipitate Group II from dilute acid solution and Group III from ammoniacal solution. In addition, it is used as a confirmatory reagent for the cations Cd^{++} , Sb^{+++} , and Zn^{++} .

Ionization of Hydrogen Sulfide.—Chemically speaking, hydrogen sulfide solution is a very weak dibasic acid (hydrosulfuric acid). It ionizes in steps,



and



The constant for the first step (primary ionization) is generally accepted to be 9×10^{-8} , and the constant for the second step (secondary ionization) 1.2×10^{-15} . The mathematical forms for these constants is

$$K_1 (\text{primary}) = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = 9 \times 10^{-8}$$

$$K_2 (\text{secondary}) = \frac{[\text{H}^+][\text{S}^{--}]}{[\text{HS}^-]} = 1.2 \times 10^{-15}$$

By multiplying these, we obtain the over-all ionization constant $K_{\text{ionisation}}$.

$$K_{\text{ionisation}} = \frac{[\text{H}^+]^2[\text{S}^{--}]}{[\text{H}_2\text{S}]} = 1.1 \times 10^{-22}$$

This expression is further simplified by taking advantage of the fact that the solubility of H_2S in aqueous solutions is practically a constant, equal to 0.1 molar at ordinary temperatures. We then have

$$K_{\text{ionisation}} = \frac{[\text{H}^+]^2[\text{S}^{--}]}{0.1} = 1.1 \times 10^{-22}$$

or

$$K_{\text{ion. prod.}} = [\text{H}^+]^2[\text{S}^{--}] = 1.1 \times 10^{-23}$$

This "ion product constant" has the form of a solubility product and is useful in calculating the solubility of sulfides in acid solutions.

Effect of Acidity on the Sulfide Ion Concentration.—A direct inference from the ion product of H_2S , as just deduced, is that the concentration of the S^{--} ion varies inversely as the square of the concentration of the H^+ ions; or, expressing it mathematically,

$$[\text{S}^{--}] \propto \frac{1}{[\text{H}^+]^2}$$

That is, the concentration of the S^{--} ions is repressed by an increase in the concentration of the H^+ ions. This is an example of the common-ion effect (page 85). Table 9 gives some representative values.

TABLE 9.—CONCENTRATION OF THE SULFIDE ION IN VARIOUS SOLUTIONS SATURATED BY H_2S

Solvent	Concentration of H^+	Concentration of S^{--}
M HCl	$0.8 M$	$1.8 \times 10^{-23} M$
$0.25 M$ HCl	0.22	2.3×10^{-22}
$0.1 M$ HCl	0.092	1.3×10^{-21}
M $\text{HC}_2\text{H}_3\text{O}_2$	0.004	6.8×10^{-18}
H_2O	9.5×10^{-5}	1.2×10^{-15}
$0.1 M$ $(\text{NH}_4)_2\text{S}$	2.5×10^{-9}	1.8×10^{-6}

Precipitation of Sulfides.—The general equation for the precipitation of the sulfide of a divalent metal M by means of H_2S is $M^{++} + \text{H}_2\text{S} \rightleftharpoons \text{MS} + 2\text{H}^+$. In equations for the precipitation of sulfides from acid solution, hydrogen sulfide is represented by the molecular formula H_2S , instead of the ionic formula S^{--} , although the latter may be the active agent. This follows the usual convention of representing weak electrolytes by their molecular formulas.

According to the solubility product principle, a sulfide will be precipitated whenever the product of the ions exceeds the

solubility product of the precipitate. Many sulfides are so insoluble that very minute concentrations of S^{--} ions are sufficient; the more soluble require fairly high concentrations.

Table 10 (column 2) shows the commonly accepted values for the solubilities of the sulfides. As in other cases of slightly soluble compounds, ionization may be assumed to be complete, so that the concentration of the S^{--} ion (column 3) may be calculated by multiplying the molar solubility by the number of S^{--} ions in the molecule. Column 4 shows the solubility products, calculated from the solubilities on the basis of complete ionization.

There is considerable doubt about the accuracy of the data in Table 10. In a few cases [indicated by (?)], the values reported in chemical literature are too uncertain for use in calculations. Though different methods give different results, it is believed that the results by any one method are comparable, so that they may be used in calculations with a fair degree of confidence. Most of the solubilities were determined by the conductivity method.

TABLE 10.—SOLUBILITIES AND SOLUBILITY PRODUCTS OF SULFIDES

Sulfide	Moles per liter	Concentration of S^{--} ion	Solubility product
As_2S_3	(?)	(?)	(?)
HgS	6.3×10^{-27}	6.3×10^{-27}	4.0×10^{-53}
CuS	9.2×10^{-23}	9.2×10^{-23}	8.5×10^{-45}
Sb_2S_3	(?)	(?)	(?)
Bi_2S_3	$3.1 \times 10^{-19} (?)$	$9.3 \times 10^{-19} (?)$	3.2×10^{-91}
SnS_2	(?)	(?)	(?)
Ag_2S	3.4×10^{-17}	3.4×10^{-17}	1.6×10^{-49}
CdS	6.0×10^{-15}	6.0×10^{-15}	3.6×10^{-29}
PbS	2.0×10^{-14}	2.0×10^{-14}	4.0×10^{-28}
SnS	(?)	(?)	(?)
CoS	1.7×10^{-13}	1.7×10^{-13}	3.0×10^{-26}
NiS	1.2×10^{-12}	1.2×10^{-12}	1.4×10^{-24}
ZnS	3.5×10^{-12}	3.5×10^{-12}	1.2×10^{-23}
FeS	3.9×10^{-10}	3.9×10^{-10}	1.5×10^{-19}
MnS	3.8×10^{-8}	3.8×10^{-8}	1.4×10^{-15}

Order of Precipitation of Sulfides.—If H_2S is introduced slowly into a solution containing the same concentrations (*e.g.*, 0.01 molar) of the cations that form insoluble sulfides, so that

the S^{--} concentration increases gradually, As_2S_3 will be the first precipitate to separate. This indicates that its solubility product is the first to be exceeded. As the S^{--} concentration continues to increase, HgS , CuS , Sb_2S_3 , Bi_2S_3 , SnS_2 , CdS , PbS , SnS , CoS , NiS , ZnS , FeS , and MnS will be precipitated in the order named. This order is determined, not by their solubility products, but rather by the concentration of the S^{--} ion in their saturated solutions. These amount to the same thing for sulfides of the same type (*e.g.*, HgS and CuS), but not for sulfides of different types (*e.g.*, CuS and Bi_2S_3). For example, the solubility product of Bi_2S_3 is much less than that of CuS ; yet the latter precipitates first (Table 10).

Selective Precipitation of Sulfides.—By proper regulation of the acidity of a solution, the concentration of the S^{--} ion may be adjusted so that the precipitation will stop at any desired point. Table 11 gives the concentrations of H^+ (*i.e.*, hydrochloric acid) at which various sulfides can be completely precipitated. These concentrations were found experimentally. The same conclusions may be reached by calculating the solubility of the sulfides in various concentrations of H^+ ions. This is done by combining the expressions for the solubility product of the sulfide and the ion product of H_2S .

TABLE 11.—CONCENTRATIONS OF HYDROCHLORIC ACID AT WHICH VARIOUS SULFIDES CAN BE PRECIPITATED

Sulfide	Concentration of acid	Sulfide	Concentration of acid
As_2S_3	12 <i>M</i>	ZnS	0.02 <i>M</i>
HgS }	7.5 <i>M</i>	CoS }	0.001 <i>M</i>
CuS }		NiS }	
Sb_2S_3	3.7 <i>M</i>	FeS }	0.0001 <i>M</i>
Bi_2S_3 }	2.5 <i>M</i>	MnS }	
SnS_2 }			
CdS	0.7 <i>M</i>		
PbS }	0.31 <i>M</i>		
SnS }			

Solubility of Sulfides in Acids.—A sulfide will dissolve in a nonoxidizing acid, such as HCl , whenever the equilibrium $MS + 2H^+ \rightleftharpoons M^{++} + H_2S$ is displaced sufficiently to the right

to more than saturate the solution with H_2S . This saturation point may be calculated by two steps. (1) The concentration of S^{--} ions prevailing in the solution is ascertained by substitution in the ion product of H_2S . (2) The concentration of M^{++} is ascertained by substituting the value of S^{--} concentration just found in the solubility product of the sulfide.

The solubility of sulfides in oxidizing acids cannot be calculated, since the reactions are not reversible and no equilibrium is involved. In such cases, solubility must be determined experimentally. See Solution in Acidic Solvents, page 107.

Examples.—1. Calculate the solubility of PbS in $0.3\ M\ \text{H}^+$. Substituting in the ion product for H_2S ,

$$\begin{aligned} [\text{H}^+]^2[\text{S}^{--}] &= 1.1 \times 10^{-23} \\ 0.3^2[\text{S}^{--}] &= 1.1 \times 10^{-23} \\ [\text{S}^{--}] &= \frac{1.1 \times 10^{-23}}{0.09} = 1.2 \times 10^{-22} \end{aligned}$$

Next, substituting in the solubility product for PbS ,

$$\begin{aligned} [\text{Pb}^{++}][\text{S}^{--}] &= 4.0 \times 10^{-28} \\ [\text{Pb}^{++}]1.2 \times 10^{-22} &= 4.0 \times 10^{-28} \\ [\text{Pb}^{++}] &= 3.3 \times 10^{-6} \text{ gram ion per liter} \end{aligned}$$

Changing from moles to grams, by multiplying by the molecular weight 239, the solubility of PbS is $3.3 \times 10^{-6} \times 239$, or 0.0009 g. per liter. This concentration is very small, and the Pb^{++} may be considered completely precipitated in Group II.

2. At what acidity will ZnS begin to form in a solution containing $0.001\ M\ \text{Zn}^{++}$?

Substituting in the solubility product for ZnS ,

$$\begin{aligned} [\text{Zn}^{++}][\text{S}^{--}] &= 1.2 \times 10^{-23} \\ 0.001[\text{S}^{--}] &= 1.2 \times 10^{-23} \\ [\text{S}^{--}] &= 1.2 \times 10^{-20} \end{aligned}$$

Next, substituting in the ion product for H_2S ,

$$\begin{aligned} [\text{H}^+]^2[\text{S}^{--}] &= 1.1 \times 10^{-23} \\ [\text{H}^+]^2 1.2 \times 10^{-20} &= 1.1 \times 10^{-23} \\ [\text{H}^+]^2 &= 0.9 \times 10^{-3}, \text{ or } 9 \times 10^{-4} \\ [\text{H}^+] &= 3 \times 10^{-2}, \text{ or } 0.03\ M \end{aligned}$$

That is, an H^+ concentration lower than $0.3\ M$ is necessary for this precipitation. Hence Zn^{++} is not precipitated in Group II.

3. What concentration of H^+ will be required to prevent the precipitation of ZnS in $0.1\ M\ \text{Zn}^{++}$ solution?

Substituting in the solubility product for ZnS ,

$$\begin{aligned} [\text{Zn}^{++}][\text{S}^{--}] &= 1.2 \times 10^{-23} \\ 0.1[\text{S}^{--}] &= 1.2 \times 10^{-23} \\ [\text{S}^{--}] &= 1.2 \times 10^{-22} \text{ (the concentration of } \text{S}^{--} \text{ at} \\ &\quad \text{which precipitation will begin)} \end{aligned}$$

Substituting this value in the ion product for H_2S ,

$$\begin{aligned} [\text{H}^+]^2[\text{S}^{--}] &= 1.1 \times 10^{-23} \\ [\text{H}^+]^2(1.2 \times 10^{-22}) &= 1.1 \times 10^{-23} \\ [\text{H}^+]^2 &= 0.90 \times 10^{-1}, \text{ or } 0.09 \\ [\text{H}^+] &= 0.3 \text{ } M \end{aligned}$$

DISSOLVING OF SULFIDE PRECIPITATES

As a rule, the precipitation of sulfides by H_2S is not readily reversible. For some reason, many sulfides are insoluble in a concentration of acid that would prevent their precipitation. CoS and NiS are the most conspicuous examples. Co^{++} and Ni^{++} are not precipitated by H_2S in the presence of $0.25 \text{ } M \text{ H}^+$, and yet when once precipitated they are apparently insoluble in even $2 \text{ } M \text{ H}^+$. Probably they do dissolve, but they dissolve very slowly. The same is true of other sulfides, but not to such a large degree.

Solution in Acidic Solvents.—The solubility of sulfides in acidic solvents is determined by their solubilities in water, *i.e.*, by the concentration of the S^{--} ions that they maintain in their saturated solution. Several types of reactions may be distinguished.

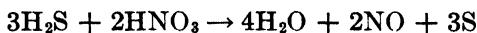
1. *Solution in Nonoxidizing Acids with the Evolution of H_2S .*—If a sulfide is soluble enough in water to maintain a S^{--} concentration of the order of 1×10^{-12} gram ion per liter, it will dissolve in $0.25 \text{ } M \text{ HCl}$, evolving H_2S . The effective ion product in this case will be

$$[\text{H}^+]^2[\text{S}^{--}] = 0.25^2 \times 10^{-12} = 6.2 \times 10^{-14}$$

which exceeds the true ion product sufficiently for gaseous H_2S to be formed rapidly. The speed of the reaction will be favored by heat, since this both increases the mobilities of the ions and reduces the solubility of the H_2S .

The most common nonoxidizing acids are hydrochloric and dilute sulfuric acids.

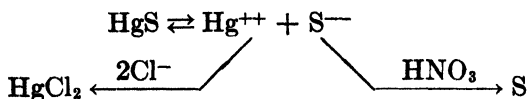
2. *Solution in Nitric Acid, with the Separation of Sulfur.*—If a sulfide is soluble enough to maintain a S^- ion concentration of the order of 1×10^{-15} gram ion per liter, it will dissolve readily in warm dilute HNO_3 (6 molar). This concentration of nitric acid is sufficient rapidly to oxidize S^- (or better, H_2S) to free sulfur.



The reduction product of dilute HNO_3 is always colorless NO . At 100° , 2 *M* HNO_3 is sufficient for this oxidation. It will be noted that HNO_3 would be expected to react with all sulfides except HgS and As_2S_3 , whose S^- ion concentrations are less than 1×10^{-25} . If concentrated HNO_3 is used, HgS is slowly attacked, and As_2S_3 completely decomposed. Brown NO_2 is always formed when concentrated HNO_3 is reduced.

3. *Solution in Aqua Regia, Forming Free Sulfur and a Stable Chloride.*—Sulfides dissolve more readily in HCl than in most other nonoxidizing acids, if the cation of the sulfide forms with Cl^- ions a molecule or a complex of low ionization. This explains why CdS is more soluble in dilute HCl than in dilute H_2SO_4 (see page 229). The product in the reaction is probably $CdCl_4^-$ and not Cd^{++} .

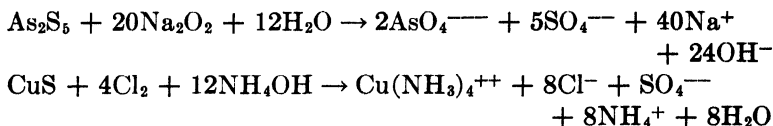
This is probably the reason why HgS dissolves readily in aqua regia. The oxidizing strength of the HNO_3 alone is not sufficient to react with the low concentration of S^- ions from HgS . And the Cl^- ion alone is not sufficient to react with the low concentration of Hg^{++} ions. But when HNO_3 and Cl^- act together, solution is rapidly effected.



The "nascent-chlorine" theory of the action of aqua regia is hardly sufficient. Hydrochloric acid is a reducing agent, reducing many oxidizing agents (*e.g.*, MnO_2 , $K_2Cr_2O_7$, etc.) and being oxidized to H_2O and Cl_2 . It does not stand to reason that a reducing agent could be mixed with an oxidizing agent with a resultant increase in oxidizing strength.

Solution in Alkaline Solvents.—Certain sulfides are soluble in alkaline sulfide solutions (*i.e.*, in S^{--} or S_x^{--}), forming complex thio anions (see page 115). This is the basis of the separation of Group II into its subgroups.

Alkaline solutions of peroxides, hypochlorites, hypobromites, etc., are powerful oxidizing agents, oxidizing sulfur to SO_4^{--} . For example,



These reactions are limited to the sulfides of elements that form amphoteric hydroxides or soluble NH_3 complexes.

Exercises

1. For what cations is H_2S used as a confirmatory reagent?
2. Compare the concentrations of S^{--} and HS^- ions in saturated H_2S solution.
3. In what respect does the ion product of saturated H_2S fail in being a true solubility product? Write an expression showing all the equilibria involved.
4. H_2S is passed into a solution .001 molar in Ag^+ and .001 molar in Cu^{++} . Which sulfide will be the first to precipitate? The solubility products are: Ag_2S , 1.6×10^{-49} ; CuS , 8.5×10^{-46} . *Ans.*: CuS .
5. Suppose a slightly acid solution containing As^{+++} , Cd^{++} , Cu^{++} , and Zn^{++} is slowly saturated with H_2S . In what order will the sulfides form? Describe the color changes involved.
6. Calculate the solubility of ZnS in M $HCl_2H_3O_2$ (0.4 per cent ionized). *Ans.*: 1.7×10^{-5} .
7. Calculate the concentration of S^{--} in a 0.2 M H^+ solution that has been saturated with H_2S .
8. Will H_2S give a precipitate with 0.001 M Zn^{++} in the presence of 0.2 M H^+ ?
9. Calculate the H^+ concentration necessary to prevent H_2S precipitating CdS from 0.004 M Cd^{++} .
10. Calculate the solubility of MnS in saturated H_2CO_3 ($[H^+] = 1 \times 10^{-6}$).
11. What must be the concentration of H^+ in a solution that is 0.0004 molar in Pb^{++} to prevent H_2S precipitating PbS ? *Ans.*: 3.3 molar.
12. Why cannot the S^{--} concentration in saturated H_2S be calculated directly from $K = 1.1 \times 10^{-22}$, assuming that the S^{--} concentration is one-half of the H^+ concentration?
13. From the primary and secondary ionization constants of H_2S , calculate the concentrations of (a) H^+ , (b) HS^- , and (c) S^{--} in 0.1 M H_2S . *Ans.*: (a) 9.5×10^{-8} , (b) 9.5×10^{-6} , (c) 1.2×10^{-14} .

14. Calculate the concentration of HS^- in a M HCl solution that has been saturated with H_2S .

15. Compare the concentrations of H^+ in $0.1 M$ H_2S and in $0.1 M$ NaHS .

16. From its solubility product, calculate the molar solubility of CdS .

17. Suppose that the solubility product of SnS_2 were known to be 3.2×10^{-53} . Calculate its molar solubility.

18. Calculate the solubility of MnS in M $\text{HC}_2\text{H}_3\text{O}_2$. Is the answer surprising?

19. What concentration of H^+ will prevent H_2S from precipitating FeS from $0.1 M$ Fe^{++} ? *Ans.*: 0.0028 molar.

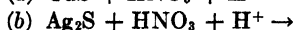
20. A solution is 0.1 molar in Zn^{++} and 0.25 molar in H^+ . What fraction of the Zn^{++} will be precipitated upon saturating the solution with H_2S in Group II? *Ans.*: 31.25 per cent.

21. What is the maximum concentration of Ni^{++} that may be present in a Group II solution, if no NiS is to be precipitated? *Ans.*: 0.008 molar.

22. Name two acids besides HCl whose dilute solutions are nonoxidizing.

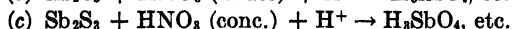
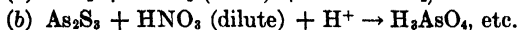
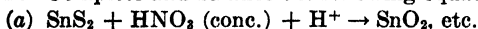
23. Assume that the formation of sulfides by H_2S is perfectly reversible, *i.e.*, that there is no false equilibrium between sulfide and S^{--} ions, or among S^{--} , H^+ , and H_2S . What would happen when any sulfide was boiled with dilute HCl ?

24. Complete and balance the following equations, assuming that the HNO_3 is dilute:

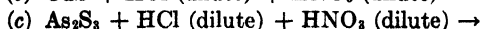
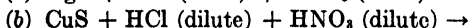
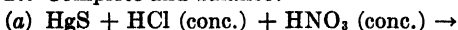


25. Complete and balance the equations in the preceding exercise, assuming that the HNO_3 is concentrated.

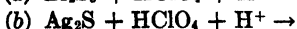
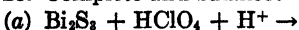
26. Complete and balance the following equations:



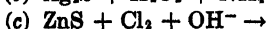
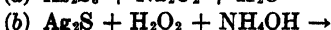
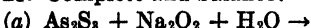
27. Complete and balance:



28. Complete and balance:



29. Complete and balance:



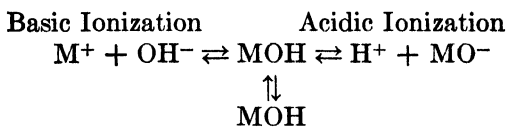
CHAPTER IX

AMPHOTERIC HYDROXIDES AND SULFIDES

Certain hydroxides show both basic and acidic properties. Toward strong acids they react as bases, and toward strong bases they react as acids. Hydroxides showing this dual behavior are called *amphoteric*, meaning that they "behave in both ways."

Certain oxides also are considered amphoteric. In the presence of water, their activity is probably due to hydroxides, formed by the hydration of the oxides. In anhydrous systems at high temperatures—*e.g.*, melts—the anhydrous forms become active, and in such cases the oxides are truly amphoteric.

Amphoteric Ionization.—Amphoterism is usually explained by assuming that hydroxides of this kind maintain in solution stocks of both OH^- and H^+ . The amounts of these ions must be small, so as not to exceed the ion product of water. These hydroxides show simultaneously two modes of ionization.



Here M is used to represent metals in general. If a strong base is added to this equilibrium mixture, its large OH^- concentration not only represses the basic ionization (common-ion effect) but also favors the acidic ionization by removing the H^+ ions. As a result, the solid hydroxide goes into solution as the MO^- anion. In an analogous way, a strong acid displaces the equilibrium leftward, since the high H^+ concentration represses the acidic ionization and removes the OH^- formed by the basic ionization. Consequently, the final product is the M^+ cation. Hydroxides showing this dual behavior are called *ampholytes*.

Water is the simplest of the amphoteric hydroxides, dissociating to a small extent into H^+ and OH^- ions. This dissociation

Arsenic hydroxide, $\text{AsO}(\text{OH})_3$
 Chromic hydroxide, $\text{Cr}(\text{OH})_3$
 Lead hydroxide, $\text{Pb}(\text{OH})_2$
 Molybdenum hydroxide, $\text{MoO}_2(\text{OH})_2$
 Stannous hydroxide, $\text{Sn}(\text{OH})_2$
 Stannic hydroxide, $\text{SnO}(\text{OH})_2$
 Tungstic hydroxide, $\text{WO}_2(\text{OH})_2$
 Uranium hydroxide, $\text{UO}_2(\text{OH})_2$
 Vanadium hydroxide, $\text{VO}(\text{OH})_3$

In addition to the preceding list, certain elements situated at a distance from the diagonal form amphoteric hydroxides. Gold and certain metals of Group VIII (*e.g.*, osmium) show this behavior to a greater extent than some of the elements already listed. $\text{Cu}(\text{OH})_2$ dissolves in concentrated NaOH solution, forming a blue liquid.

Effect of Valence.—It seems to be a general rule that the acidic nature of an element increases with its valence. H_2SO_4 is a stronger acid than H_2SO_3 , and HNO_3 is a stronger acid than HNO_2 . From this it is to be expected that stannic acid, H_2SnO_3 , should be stronger than stannous acid, H_2SnO_2 , and arsenic acid, H_3AsO_4 , than arsenious acid, H_3AsO_3 . Chromic hydroxide, $\text{Cr}(\text{OH})_3$, is only faintly acidic, and chromic acid, H_2CrO_4 , is a strong acid, with no appreciable basic properties.

Nomenclature.—The nomenclature of the molecules and ions involved in the acidic ionization of the amphoteric hydroxides

Basic formula	Acidic formula	Anions
$\text{Al}(\text{OH})_3$	H_3AlO_3 , aluminic acid	AlO_2^- , aluminate (meta)
$\text{SbO}(\text{OH})_3$	H_3SbO_4 , antimonie acid	H_2SbO_4^- , antimonate
$\text{SbO}_2(\text{OH})$	HSbO_3 , metaantimonie acid	SbO_3^- , metaantimonate
$\text{Sb}(\text{OH})_3$	H_3SbO_3 , antimonious acid	SbO_2^- , antimonite (meta)
$\text{AsO}(\text{OH})_3$	H_3AsO_4 , arsenic acid	AsO_4^{--} HAsO_4^{--} H_2AsO_4^-
		} arsenate
$\text{As}(\text{OH})_3$	H_3AsO_3 , arsenious acid	AsO_2^- , arsenite (meta)
$\text{Pb}(\text{OH})_2$	H_2PbO_2 , plumbous acid	HPbO_2^- , plumbite
$\text{Sn}(\text{OH})_4$	H_2SnO_3 , stannic acid	HSnO_3^- , stannate (meta)
$\text{Sn}(\text{OH})_2$	H_2SnO_2 , stannous acid	HSnO_2^- , stannite
$\text{Zn}(\text{OH})_2$	H_2ZnO_2 , zincic acid	HZnO_2^- , zincate

follows the usual convention for that of the oxyacids and their salts. According to the valence of the element, the hydroxides are considered "ic" or "ous" acids, and the corresponding anions "ates" and "ites." Note the tabulation at foot of page 113.

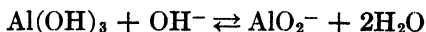
Limited Ionization.—As stated above, amphoteric hydroxides are very weak bases and acids. Their ionization is of the order of that of water. Consequently, their acid ionization is limited to a single H atom (primary ionization), giving "acid" anions; *e.g.*,



Considering the anions of amphoteric hydroxides as having the "acid" formula is not in line with common usage. For example, sodium stannite is generally considered Na_2SnO_2 , and sodium arsenite Na_3AsO_3 . Such formulas are now regarded as incorrect, but their use is continued because the "normal" forms appear simpler and because, in certain cases, normal salts have been prepared in the dry form. The solutions of these normal salts, however, contain not normal ions, but hydro-ions. The case is exactly similar to that of sodium sulfide. Solutions of Na_2S contain almost no S^{--} ions, but rather SH^- and OH^- ions, as follows: $\text{S}^{--} + \text{HOH} \rightleftharpoons \text{SH}^- + \text{OH}^-$. This is a simple case of hydrolysis (see pages 129 to 133). It is troublesome to unlearn erroneous formulas, but the chemist should prefer to know things as they are, instead of as he would like them to be.

Solubility of Amphoteric Hydroxides in Ammonium Hydroxide.

Amphoteric hydroxides are slightly soluble in NH_4OH solution, to a degree determined by the concentration of the OH^- ion. Illustrating by $\text{Al}(\text{OH})_3$, we have the equilibrium

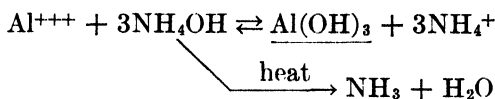


Applying the mass law,

$$\frac{[\text{AlO}_2^-][\text{H}_2\text{O}]^2}{[\text{Al}(\text{OH})_3][\text{OH}^-]} = \text{constant}$$

This expression may be simplified by dropping $[\text{H}_2\text{O}]$ and $[\text{Al}(\text{OH})_3]$, since the water is present in large excess and $\text{Al}(\text{OH})_3$ as a saturated solution, so that their concentrations are practically constant (see pages 50 and 90). We then have $[\text{AlO}_2^-]/[\text{OH}^-] = \text{constant}$, or $[\text{AlO}_2^-] \propto [\text{OH}^-]$. The concentration of the AlO_2^- ion is therefore a measure of the solubility of the $\text{Al}(\text{OH})_3$. Since the OH^- concentration in NH_4OH is large compared with that

in water, the solubility in NH_4OH becomes appreciable. If it is desired to precipitate any amphoteric hydroxide completely, using NH_4OH as a precipitant, a large excess of NH_4OH must be avoided. This may be done by adding NH_4OH to a hot solution, when the excess of NH_4OH will be expelled as NH_3 . The solution must not be boiled after adding the NH_4OH ; for the reaction will be reversed owing to the escape of NH_3 , and the precipitation will be incomplete. For example,



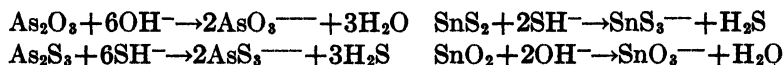
Buffering by the presence of an excess of NH_4^+ salts will repress the tendency toward solution, but the practice of "loading" a solution with NH_4^+ ions is bad, for excess of NH_4^+ interferes with certain subsequent reactions.

Amphoteric Sulfides.—Sulfur and oxygen belong to Group VI of the Periodic Table, and a certain resemblance in properties is therefore to be expected. There is a definite analogy between H_2O and H_2S , and sulfur frequently "substitutes" for oxygen, forming thio compounds; *e.g.*,

Na_2SO_4 , sodium sulfate $\text{Na}_2\text{S}_2\text{O}_3$, sodium thiosulfate
 K_3AsO_4 , potassium arsenate . . . K_3AsS_4 , potassium thioarsenate
 $(\text{NH}_2)_2\text{CO}$, urea $(\text{NH}_2)_2\text{CS}$, thiourea
 $\text{C}_2\text{H}_5\text{OH}$, ethyl alcohol $\text{C}_2\text{H}_5\text{SH}$, ethyl thioalcohol

It should be noted in the above examples that the valence of sulfur is -2 . There is no analogy for other valences of sulfur.

A strong similarity is found between these elements in their formation of amphoteric hydroxides and hydrosulfides. Most elements that form amphoteric hydroxides also form amphoteric sulfides. (Exceptions will be noted later.) For example,



The nomenclature of the amphoteric thio acids and their salts is parallel to that of the amphoteric hydroxides.

Sulfide	Acidic formula	Anion
As_2S_3	$[\text{H}_3\text{AsS}_3]$ thioarsenious acid	AsS_3^{---} thioarsenite
As_2S_5	$[\text{H}_3\text{AsS}_4]$ thioarsenic acid	AsS_4^{---} thioarsenate
Sb_2S_3	$[\text{H}_3\text{SbS}_3]$ thioantimonious acid	SbS_3^{---} thioantimonite
Sb_2S_5	$[\text{H}_3\text{SbS}_4]$ thioantimonic acid	SbS_4^{---} thioantimonate
SnS_2	$[\text{H}_2\text{SnS}_3]$ thiostannic acid	SnS_3^{--} thiostannate

The thio acids show the same increase in strength with increase in valence as that shown by the oxyacids. Thiostannic acid, H_2SnS_3 , is a stronger acid than thiostannous acid, H_2SnS_2 ; and thioantimonic acid, H_3SbS_4 , is a stronger acid than thioantimonious acid, H_3SbS_3 . This is shown by the relative solubilities of the sulfides of the Tin subgroup in colorless ammonium sulfide, $(\text{NH}_4)_2\text{S}$ (page 222).

For some unknown reason, PbS and ZnS are not amphoteric, while the corresponding hydroxides are. The same is true of SnS . The truly amphoteric sulfides belong to the Tin subgroup. They are As_2S_3 and As_2S_5 , Sb_2S_3 and Sb_2S_5 , and SnS_2 .

Exercises

1. Name two metals besides zinc that dissolve in alkali solutions with the liberation of hydrogen.
2. When metals dissolve in NaOH solution with the liberation of hydrogen, does the NaOH function as an acid?
3. Write formulas for the following salts of amphoteric hydroxides:

Zinc aluminate
 Ferric arsenate
 Magnesium arsenite

Copper zincate
 Barium chromite
 Lead antimonate

The soluble salts of amphoteric hydroxides, owing to extensive hydrolysis, do not have definite formulas.

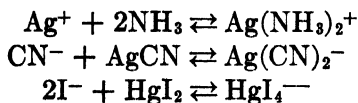
4. Suppose Na_2SnO_2 did exist in dry form. What would be the probable composition of its solution?

5. Formulate the equilibriums existing in a mixture of AlCl_3 and NH_4OH solutions.
6. Name two metals whose hydroxides are amphoteric and whose sulfides are not amphoteric.
7. Which is more acidic, SnS or SnS_2 ? Cite reactions to support your opinion.
8. Write equations for the acidification of the following thio anions: AsS_3^{--} , AsS_4^{--} , SbS_2^- , SnS_3^{--} . Compare with the equations for the corresponding oxy anions.
9. What anions are present in a solution of Na_3AsS_4 ? What reaction would occur if Pb^{++} were added to such a solution?

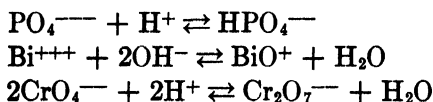
CHAPTER X

COMPLEX IONS. INSTABILITY CONSTANTS

Complex ions are formed in two ways, *viz.*: (1) the combination of an ion with a neutral molecule; (2) the combination of an ion with another ion. Examples of the first type are



The most common examples of the second class are found in the formation of acid or basic ions by the addition of H^+ or OH^- ; *e.g.*,



Probably there are no simple ions in the original sense of the term. Ions are now assumed to be hydrated (page 56), so that even the hydrogen ion is not a simple ion, but a complex, $\text{H}\cdot\text{H}_2\text{O}^+$; the cupric ion is not Cu^{++} , but a hydrate, possibly $\text{Cu}\cdot 4\text{H}_2\text{O}^{++}$. In such cases, however, there is no advantage in including the water of hydration in equations, and so the old usage of writing the "simple" ions as anhydrous will be continued.

Complex ions play an important part in analytical practice. Two substances may be separated by adding a reagent that will form a soluble complex ion with one of them, but not with the other. For example, AgCl is extracted from Hg_2Cl_2 by adding NH_4OH , which forms a soluble complex ion with AgCl , but not with Hg_2Cl_2 . The student should watch for other applications of this principle.

Instability Constant.—Complex ions dissociate, more or less, into their constituents. For example, if M is a metal and X an

anion, forming the complex ion, MX_2^- , then $\text{MX}_2^- \rightleftharpoons \text{M}^+ + 2\text{X}^-$. Applying the mass law,

$$\frac{[\text{M}^+][\text{X}^-]^2}{[\text{MX}_2^-]} = K$$

This particular equilibrium constant has been called the *instability constant*, since it is a measure of the instability of the complex ion; *i.e.*, the greater the degree of dissociation, the larger the constant. It is usually indicated by $K_{\text{instability}}$.

Instability constants may be determined in two ways: (1) The solubility of a slightly soluble salt of known solubility product is measured in the complexing solution, *e.g.*, AgCl in a definite concentration of NH_3 . (2) The concentration of the "simple" ion in equilibrium with the complex is determined by e.m.f. measurements (see textbooks on physical chemistry for details).

TABLE 12.—INSTABILITY CONSTANTS

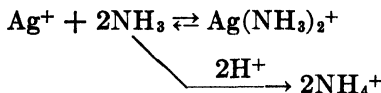
$\frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = 6.8 \times 10^{-8}$	$\frac{[\text{Hg}^{++}][\text{Cl}^-]^4}{[\text{HgCl}_4^{--}]} = 6.0 \times 10^{-17}$
$\frac{[\text{Cd}^{++}][\text{NH}_3]^4}{[\text{Cd}(\text{NH}_3)_4^{++}]} = 1.0 \times 10^{-7}$	$\frac{[\text{Hg}^{++}][\text{Br}^-]^4}{[\text{HgBr}_4^{--}]} = 2.2 \times 10^{-22}$
$\frac{[\text{Zn}^{++}][\text{NH}_3]^4}{[\text{Zn}(\text{NH}_3)_4^{++}]} = 2.6 \times 10^{-10}$	$\frac{[\text{Hg}^{++}][\text{I}^-]^4}{[\text{HgI}_4^{--}]} = 5.0 \times 10^{-31}$
$\frac{[\text{Cu}^{++}][\text{NH}_3]^4}{[\text{Cu}(\text{NH}_3)_4^{++}]} = 1.0 \times 10^{-7}$	$\frac{[\text{Hg}^{++}][\text{CN}^-]^4}{[\text{Hg}(\text{CN})_4^{--}]} = 4.0 \times 10^{-41}$
$\frac{[\text{Cu}^+][\text{CN}^-]^4}{[\text{Cu}(\text{CN})_4^{--}]} = 5.0 \times 10^{-28}$	$\frac{[\text{Hg}^{++}][\text{SCN}^-]^4}{[\text{Hg}(\text{SCN})_4^{--}]} = 1.0 \times 10^{-22}$
$\frac{[\text{HgCl}_2][\text{Cl}^-]^2}{[\text{HgCl}_4^{--}]} = 1.0 \times 10^{-2}$	$\frac{[\text{Ag}^+][\text{S}_2\text{O}_3^{--}]}{[\text{AgS}_2\text{O}_3^-]} = 1.0 \times 10^{-13}$
$\frac{[\text{Ag}^+][\text{CN}^-]^2}{[\text{Ag}(\text{CN})_2^-]} = 1.0 \times 10^{-21}$	

Some representative instability constants are shown in Table 12.

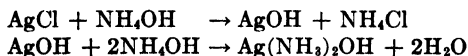
Ammonia Complex Ions.—A number of cations combine with the NH_3 present in NH_4OH solution to form complex ammonia cations (sometimes called *ammines*).

The Silver Ammonia Complex Ion.—The Ag^+ ion unites with NH_3 molecules, forming the $\text{Ag}(\text{NH}_3)_2^+$ ion. The reaction is slightly reversible. The ion dissociates enough to give a suffi-

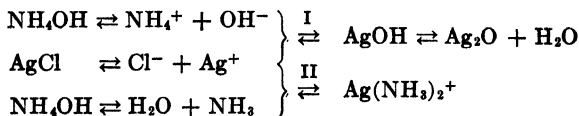
cient concentration of NH_3 to react with the H^+ ions of acids, completely reversing the action.



The solution of silver compounds in NH_4OH is sometimes represented by two consecutive equations; *e.g.*,



This representation is not correct, if it implies that the silver must pass through the AgOH stage in order to become $\text{Ag}(\text{NH}_3)_2^+$. The temporary formation of AgOH is wholly incidental, owing to the fact that there are, in the early stages of the reaction, sufficient Ag^+ and OH^- ions to exceed the solubility product of AgOH , so that partial precipitation takes place (equilibrium I, below). But the concentrations of these two ions diminish rapidly, owing to the Ag^+ being used up to form $\text{Ag}(\text{NH}_3)_2^+$, and the OH^- being repressed by increasing concentrations of NH_4^+ as more of the reagent is added. At the same time, the concentration of NH_3 is increasing rapidly, favoring the formation of $\text{Ag}(\text{NH}_3)_2^+$ (equilibrium II).



The error in the consecutive equations given above may be shown experimentally by a titration. If 10 cc. of 0.1 M AgNO_3 is converted into AgCl (*e.g.*, by an excess of NaCl solution), it takes exactly 20 cc. of 0.1 M NH_4OH to dissolve the precipitate. This shows a 1:2 ratio between Ag^+ and NH_3 . When the preceding equations are added, there is obtained



This equation would call for a 1:3 ratio between Ag^+ and NH_4OH .

The utility of the instability constant is illustrated in the following exercises.

Calculation of the Ag^+ Concentration in a NH_4OH Solution.—Suppose that $\frac{1}{10}$ mole of AgCl is dissolved in 1 l. of 0.3 M NH_4OH . Two-tenths mole of NH_4OH would be used up in converting the AgCl into $\text{Ag}(\text{NH}_3)_2^+$, leaving the NH_4OH solution 0.1 molar. The concentration of the $\text{Ag}(\text{NH}_3)_2^+$ ion

will also be 0.1 molar (not counting the trace of Ag^+ in the mixture). Substituting in the instability constant for $\text{Ag}(\text{NH}_3)_2^+$,

$$\frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = \frac{[\text{Ag}^+] \times 0.1^2}{0.1} = 6.8 \times 10^{-8}$$

Solving

$$\text{Ag}^+ = 6.8 \times 10^{-7}$$

Solubility of the Silver Halides in NH_4OH .—Suppose that AgCl is shaken with 1 l. of 0.1 M NH_3 solution until the latter is saturated with the salt. The silver is present in the solution almost wholly as $\text{Ag}(\text{NH}_3)_2^+$, so that the concentration of this ion may be taken as a measure of the solubility. This concentration can be evaluated in terms of the concentration of NH_3 as follows:

In the reaction $\text{AgCl} + 2\text{NH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+ + \text{Cl}^-$, equivalent amounts of $\text{Ag}(\text{NH}_3)_2^+$ and Cl^- are formed, so that $[\text{Cl}^-] = [\text{Ag}(\text{NH}_3)_2^+]$. Dividing the instability constant for $\text{Ag}(\text{NH}_3)_2^+$ by the solubility product of AgCl ,

$$\frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = \frac{6.8 \times 10^{-8}}{1.2 \times 10^{-10}}$$

Simplifying,

$$\frac{[\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]} = 5.7 \times 10^2$$

Since $[\text{Cl}^-] = [\text{Ag}(\text{NH}_3)_2^+]$,

$$\begin{aligned} \frac{[\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]^2} &= 5.7 \times 10^2 \\ \frac{[\text{NH}_3]}{[\text{Ag}(\text{NH}_3)_2^+]} &= 2.4 \times 10, \text{ or } 24 \end{aligned}$$

If x = number of moles of AgCl dissolved, then x = number of moles of $\text{Ag}(\text{NH}_3)_2^+$ formed, and the final concentration of NH_3 is $(0.1 - 2x)$. Substituting and solving,

$$\frac{0.1 - 2x}{x} = 24$$

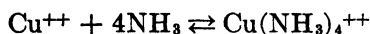
$x = 0.00384$, the solubility (moles per liter) of AgCl in 0.1 M NH_3 .

In the cases of AgBr and AgI , their solubilities in NH_4OH are so slight that the calculation may be simplified by assuming that the final concentration of NH_3 does not differ sensibly from the original. In such cases, the solubilities may be calculated by substituting in the last of the above equations the total value of $[\text{NH}_3]$.

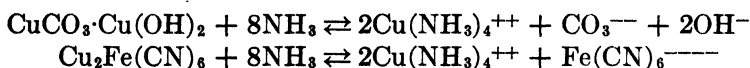
$$\frac{[\text{NH}_3]}{[\text{Ag}(\text{NH}_3)_2^+]} = \frac{6.8 \times 10^{-8}}{K_{\text{sol. prod.}}}$$

The solubility products of AgBr and AgI are 3.5×10^{-13} and 1.7×10^{-16} , respectively. Assuming that the final value of $[\text{NH}_3]$ approximates 0.1, and substituting and solving, the following solubilities are obtained: AgBr, 0.00023 mole per liter; AgI, 0.00005 mole per liter.

Copper Ammonia Complex Ions.—Cupric ions combine with four NH_3 molecules, forming the deep blue cupric ammonia ion $\text{Cu}(\text{NH}_3)_4^{++}$.



This complex ion has a moderate stability, much less than that of the cyanide complex (see Table 12). Ammonia solution will dissolve $\text{Cu}(\text{OH})_2$ and $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, and even $\text{Cu}_2\text{Fe}(\text{CN})_6$, but not the very insoluble CuS .



Cuprous ions, Cu_2^{++} , form the colorless cuproammonia ion—possibly $\text{Cu}_2(\text{NH}_3)_4^{++}$ or $\text{Cu}(\text{NH}_3)_2^+$. For example, cuprous chloride is readily soluble in NH_4OH solution:

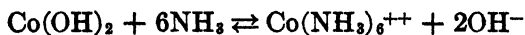


Cadmium Ammonia Complex Ion.—Cadmium ions form the colorless complex ion $\text{Cd}(\text{NH}_3)_4^{++}$; *e.g.*,



This complex is only moderately stable, being completely decomposed by H_2S , forming CdS .

Cobalt Ammonia Complex Ions.—The cobalt ions form several complex ions with NH_3 , the NH_3 content ranging from one to six. In most respects, the pentammine (*i.e.*, five NH_3 groups) seems to be the most stable. It is customary, however, to represent these amines as hexammines. For example, cobaltous hydroxide dissolves in NH_4OH , forming the yellowish cobaltous hexammine ion.



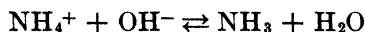
This cobaltous ammine is readily oxidized by air to the trivalent cobaltic ammine, which is brown.



As_2S_3 in NH_4OH is probably due to the formation of NH_3 complexes of unknown constitution.

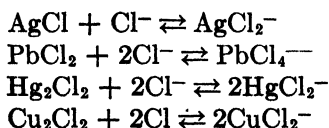
The generalization that the number of NH_3 groups entering into an ammonia complex ion is twice the valence of the cation is correct in most cases but fails in the cases of H^+ , Co^{++} , and Ni^{++} . Furthermore, there are many solid ammino salts to which the rule does not apply, *e.g.*, $\text{AgCl} \cdot 3\text{NH}_3$.

Effect of the Presence of NH_4^+ Ion.—The solvent action of NH_4OH on insoluble compounds of silver, copper, cobalt, nickel, etc., is increased in a considerable degree by the presence of NH_4^+ salts. Probably this increase in solvent action is due to a repression of the ionization of NH_4OH , forming more NH_3 molecules.



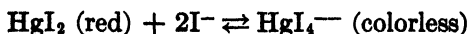
It is also possible that complex ammonium ions are formed, like $\text{Cu}(\text{NH}_4)_2^{++++}$ or $\text{Fe}(\text{NH}_4)_2^{++++}$, but there is insufficient evidence to support such a theory.

Complex Halogen Ions.—Insoluble chlorides are soluble in high concentrations of Cl^- ions. The most important cases are the following:

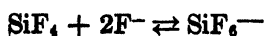


Many other complex chloro-ions are known; *e.g.*, chloroplatinate, PtCl_6^- ; chlorostannate, SnCl_6^- ; etc. Certain chlorides are less ionized than the corresponding nitrates and for this reason are less hydrolyzed. This stability is possibly due to the fact that the cation unites with excess Cl^- ions to form stable complex chloro-ions, such as SbCl_4^- , FeCl_6^{--} (possibly) and CoCl_4^{--} .

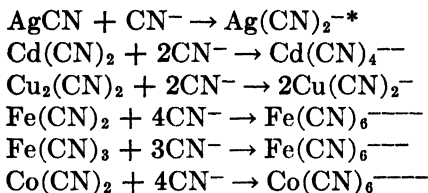
Similarly, Br^- and I^- form complex ions. Perhaps the most important is HgI_4^- , formed when HgI_2 is dissolved in an excess of I^- ions.



Another case is the formation of fluosilicate, SiF_6^- .

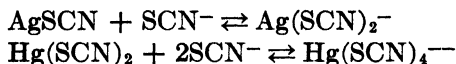


Cyanide Complex Ions.—Many insoluble cyanides (and other salts) are soluble in NaCN or KCN solution, owing to the formation of complex cyanide ions. For example,



Some of these complex cyanides (*e.g.*, $\text{Fe}(\text{CN})_6^{--}$) are very stable—decomposed only by such powerful reagents as hot H_2SO_4 , NaOH, or KOH.

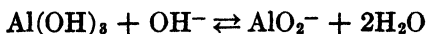
Complex Thiocyanate Ions.— SCN^- resembles the halide ions in most of its reactions. This behavior has led to its being called a *halogenoid* (halogen-like) *ion*. In line with this, we find that many insoluble thiocyanates are soluble in excess of SCN^- ions; *e.g.*,



A very interesting recent discovery is that the red color in the test for Fe^{+++} ions is due not to $\text{Fe}(\text{SCN})_3$ molecules but to $\text{Fe}(\text{SCN})_6^{--}$ ions. The $\text{Hg}(\text{SCN})_4^{--}$ is more stable than the ferric complex. This is shown by the decolorization of $\text{Fe}(\text{SCN})_6^{--}$ upon the addition of Hg^{++} .

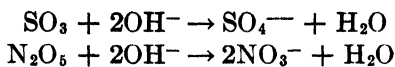
Complex Sulfide Ions.—Certain sulfides (As_2S_3 , As_2S_5 , Sb_2S_5 , and SnS_2) dissolve in excess S^{--} ions, forming complex thio ions. This behavior has been discussed under amphoteric sulfides (pages 115 and 116).

Complex Oxygen Ions.—Mention has already been made of the theory that the solubility of amphoteric hydroxides in strong bases is due to the formation of complex ions; *e.g.*,



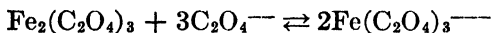
There is no reason why this theory might not be extended to cover all the oxygen-containing ions; *e.g.*,

* A single arrow, \rightarrow , is used in these reactions since their reversibility is exceedingly small.



These equations are written with single arrows since the complex ions formed are very stable.

Complex Oxalate Ions.—Certain insoluble oxalates are soluble in an excess of $\text{C}_2\text{O}_4^{--}$ ions; *e.g.*,



Complex Tartrate Ions.—Many cations form stable complexes with $\text{C}_4\text{H}_4\text{O}_6^{--}$ ions. In the list may be mentioned Cu^{++} , Fe^{+++} , Al^{+++} , Cr^{+++} , and the cations of the rare earths.

In conclusion, it should be noted that the property of forming complex ions is conspicuous in organic anions and anions containing sulfur.

The list of complex ions may be more extensive than indicated in the above discussion. For example, it is possible that the solubility of PbSO_4 in $\text{C}_2\text{H}_3\text{O}_2^-$ solutions is due to the formation of complex ions [possibly $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4^{--}$], instead of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ molecules, as generally represented. Indeed, there is reason to believe that some of the abnormalities in strong electrolytes may be due to the existence of complex ions in concentrated solutions.

Exercises

1. When NH_4OH is added to AgNO_3 solution, a precipitate first forms and then redissolves. Explain fully.

2. Refer to the preceding pages, and compare the numerical values for the solubilities of the silver halides in NH_4OH .

3. Compare the instability constants of $\text{Cd}(\text{NH}_3)_4^{++}$ and $\text{Zn}(\text{NH}_3)_4^{++}$. Which complex is more stable?

4. Calculate the solubility of CuS in M NH_3 solution.

Ans.: 3×10^{-10} molar.

5. Calculate the solubility of AgBr in $0.1 M$ $\text{S}_2\text{O}_3^{--}$, if the solubility product of AgBr is 3.6×10^{-13} .

Ans.: 0.6 mole per liter.

6. Calculate the solubility of Ag_2S in $0.1 M$ CN^- , if the solubility of Ag_2S is 1.6×10^{-49} . Recall the cyanide process for extracting silver and gold from sulfidic ores.

7. Name some complex thio anions formed by the Tin subgroup.

8. Which complex would you expect to be more stable, cupricyanide or cuprocyanoide? Relate this to the rule that the stability of an anion increases with the valence of the element.

9. Ferric solutions are decolorized by PO_4^{--} ions. Suggest an explanation.

10. Why is SbCl_3 only partially hydrolyzed, while $\text{Sb}(\text{NO}_3)_3$ is completely hydrolyzed?

11. Why will $\text{Cr}_2\text{O}_7^{--}$ give a precipitate with $\text{Hg}(\text{NO}_3)_2$ solution but not with HgCl_2 solution?

12. H_2S will not precipitate CdS from a solution of CdCl_2 that has been saturated with NaCl . Explain.

13. Why is HgS more soluble in aqua regia than in HNO_3 of the same H^+ concentration?

14. What is the formula for anhydrous ferric chloride?

15. When concentrated CdI_2 is electrolyzed, toward which electrode does the cadmium move?

16. What complex ion does Fe^{+++} form with SCN^- ?

17. Which appears to form more stable complex ions, chlorine or iodine?

18. What is the formula for solid sodium chloride?

19. Look up the definition for polymerization.

CHAPTER XI

IONIZATION OF WATER. HYDROLYSIS

Formerly chemists liked to think of water as being chemically inert, as simply supplying the medium or "atmosphere" in which reactions take place. It now appears that the solvent water is much more than an atmosphere. It actually seems to combine with the reactants (solvation), making them chemically active. Usually it does not appear in the equations as written, because it undergoes no chemical decomposition. There are cases, however, in which water appears as one of the reactants in the equation and undergoes definite chemical changes.

Ionization of Water.—Water is generally considered a non-conductor of the electric current and, for that reason, un-ionized. This is not exactly true; for the purest water that can be prepared shows a small conductivity, indicating an ionization of 1.8×10^{-7} per cent at 25° . From this it is calculated that the concentration of H^+ and OH^- in water at that temperature must be 0.0000001 (*i.e.*, 1×10^{-7}) each. The concentration of water (*i.e.*, moles per liter) has been calculated to be about 55.5 (page 50). The ionization constant for water should therefore be

$$K_{\text{ionisation}} = \frac{[H^+][OH^-]}{[H_2O]} = \frac{0.00000001 \times 0.00000001}{55.5} = 1.8 \times 10^{-16}$$

This expression may be simplified by considering $[H_2O]$ a constant, equal to 55.5. The expression then becomes

$$K = [H^+][OH^-] = 0.00000001 \times 0.00000001 = 1 \times 10^{-14}$$

This second K is 55.5 times as large as $K_{\text{ionisation}}$, and must not be confused with it. It is called the *ion product* of water and is designated as " K_{water} " or " K_{H_2O} ." It is extensively used in the calculations of hydrolysis.

Effect of Temperature.—The degree of ionization of water increases with the temperature (see Table 13).

TABLE 13.—EFFECT OF TEMPERATURE ON THE IONIZATION OF WATER

Temperature	Fraction ionized	Ion product
0°	0.33×10^{-7}	0.12×10^{-14}
10°	0.53×10^{-7}	0.28×10^{-14}
18°	0.77×10^{-7}	0.59×10^{-14}
25°	1.02×10^{-7}	1.04×10^{-14}
50°	2.40×10^{-7}	5.66×10^{-14}
100°	7.60×10^{-7}	58.20×10^{-14}

This is to be expected, since the reaction between H^+ and OH^- is highly exothermic: $H^+ + OH^- \rightarrow H_2O + 13,700$ calories. According to the Le Châtelier principle (page 48), an increase in temperature tends to reverse the reaction, favoring increased ionization. This increase in the ionization of water at higher temperatures, giving larger concentrations of H^+ and OH^- , is very important in hydrolytic reactions.

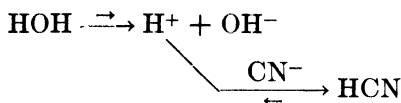
HYDROLYSIS

Solutions of certain salts are acid in reaction, and solutions of certain others are alkaline. This was formerly explained by saying that the salt was decomposed by water (hydrolysis) forming free base and free acid and that the reaction of the solution was determined by the stronger of the two.

The ionization theory gives a more logical and satisfactory explanation. While the ionization of water is negligible in most cases, it may become conspicuous when some substance is present that will combine with either the H^+ or the OH^- ions. Certain cations will combine with the OH^- ions, leaving the excess of H^+ in the solution. Certain anions will combine with the H^+ ions, leaving an excess of OH^- in the solution. So it turns out that, instead of the salt being attacked by the water, the water is attacked by the salt. The reaction is a decomposition of water, not a decomposition by water, as the term *hydrolysis* originally signified. The name *hydrolysis* will doubtless be retained, in spite of any error in etymology.

Hydrolysis of Salts.—The hydrolytic reactions of salts may be illustrated as follows:

Salt of Strong Base and Weak Acid.—Suppose that we consider a solution of potassium cyanide, KCN. Here the CN^- ion tends to combine with the H^+ ion of the water, removing it from the equilibrium as the very slightly ionized molecule HCN.



In order to maintain the constancy of the ion product of water, the concentration of the OH^- must increase as that of the H^+ ion decreases. The concentration of H^+ in 0.1 M KCN may be calculated (see latter part of this chapter) to be 9×10^{-11} at 25° . This calls for a corresponding increase in the OH^- ion concentration, for $[\text{H}^+][\text{OH}^-]$ must equal 1×10^{-14} . Substituting in this expression,

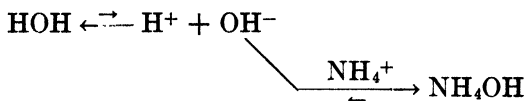
$$9 \times 10^{-11} \times [\text{OH}^-] = 1 \times 10^{-14}$$

or

$$[\text{OH}^-] = 1.1 \times 10^{-3}$$

Such a solution reacts decidedly basic. The equation may be briefly written thus: $\text{CN}^- + \text{HOH} \rightarrow \text{HCN} + \text{OH}^-$.

Salt of Weak Base and Strong Acid.—The OH^- ions in the water equilibrium may be removed by adding some cation that will combine with them to form a weak base, e.g., NH_4^+ .

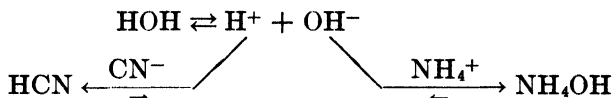


In M NH_4NO_3 solution, the concentration of the OH^- ion is reduced in this way to 4×10^{-10} , and the concentration of the H^+ ion is increased to 2.5×10^{-5} . The solution is therefore slightly acidic. Here the equation is $\text{HOH} + \text{NH}_4^+ \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+$.

In these cases, it should be noticed that the amount of hydrolysis increases with the weakness of the electrolyte formed. Hydrocyanic acid is much weaker than ammonium hydroxide, and the cyanides are hydrolyzed correspondingly more than ammonium salts. The hydrolysis of KCN produces

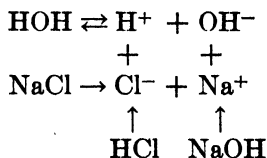
a solution almost as caustic as the equivalent amount of KOH. Ammonium salts, on the other hand, are weakly acidic but yet acidic enough to react with certain metals, *e.g.*, zinc with NH_4Cl in the so-called *dry cell*.

Salt of Weak Base and Weak Acid.—Here a greater degree of hydrolysis is to be expected than in salts where only one component is weak. In NH_4CN solution, for example, we have two agencies operating to shift the water equilibrium.

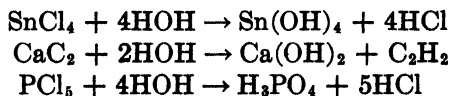


These agencies, through their teamwork, are almost sufficient to tie up all the ions from NH_4CN as HCN and NH_4OH . The equation is $\text{HOH} + \text{NH}_4^+ + \text{CN}^- \rightarrow \text{NH}_4\text{OH} + \text{HCN}$.

Salt of Strong Base and Strong Acid.—There is no hydrolysis in this case. Owing to the high ionization of the base and acid, there is no tendency to withdraw H^+ and OH^- from the water equilibrium, and the relative amounts of these ions are unchanged. Consequently, solutions of salts of this type are neutral, *e.g.*, NaCl , KNO_3 , etc. In the following diagram for NaCl solution, note that the arrows indicate the complete dissociation of base and acid:

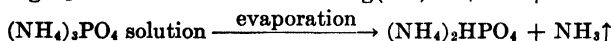
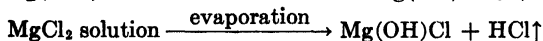
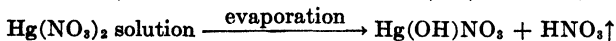
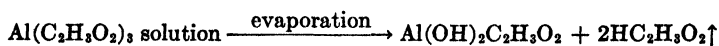


Complete Hydrolysis.—If either component of the salt is exceedingly weak, and especially if one of them is volatile, the compound may be completely (irreversibly) hydrolyzed. Under this heading fall many saltlike compounds, such as stannic chloride, calcium carbide and the chlorides of phosphorus.



Many other compounds, more truly saltlike in nature, give basic

salts upon evaporation, although their hydrolysis is not complete. For example:



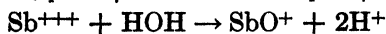
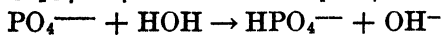
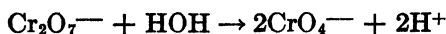
Such salts may be re-formed by treating the residues with an excess of the acid or base lost by volatilization.

Products of Hydrolysis.—From the preceding paragraph it is seen that the products of hydrolysis may be free base and free acid, or basic or acidic salt. The influence determining the product is usually insolubility. Bismuth salts, for example, are hydrolyzed to the bismuthyl ion BiO^+ , which forms very insoluble salts with most anions. Consequently, the hydrolytic products are basic salts, and not $\text{Bi}(\text{OH})_3$, as might be expected.

Sometimes a salt seems to undergo progressive hydrolysis. Since ionization is a stepwise process, each of the intermediate ions obtained should be able to combine with OH^- or H^+ , as the case may be. The basic bismuth salts mentioned above when heated with an excess of water approximate $\text{Bi}(\text{OH})_3$ as the end product. Perhaps the following steps exist: $\text{BiCl}_3 \rightarrow \text{Bi}(\text{OH})\text{Cl}_2 \rightarrow \text{Bi}(\text{OH})_2\text{Cl}$ (or BiOCl) $\rightarrow \text{Bi}(\text{OH})_3$. Ferric acetate, upon boiling with excess of water, undergoes an indefinite amount of hydrolysis, the final product being approximately $\text{Fe}(\text{OH})_2\text{C}_2\text{H}_3\text{O}_2$. Definite composition seems unattainable.

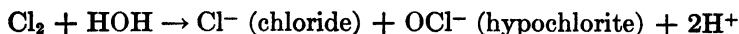
Other Types of Hydrolysis.—The term hydrolysis is extended to other types of reactions.

Hydrolysis of Ions.—The hydrolysis of the Bi^{+++} ion, forming BiO^+ , has already been mentioned. Other cases¹ of the hydrolysis of ions may also be mentioned.



¹ The hydration of meta- and pyro-salts, forming ortho-salts, is probably a true case of hydrolysis, in which both the H^+ and the OH^- ions are added to the same ion; e.g., PO_3^{--} (metaphosphate anion) $+ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{PO}_4^{--}$ (orthophosphate).

Hydrolysis of Halogens.—Free halogens are hydrolyzed by water, forming a halide ion and a hypohalite ion; *e.g.*,



Cyanogen and analogous compounds behave similarly.

Decomposition by Water.—Certain compounds seem to be actually decomposed by water in a way that meets the original definition of the term. These reactions differ from ordinary hydrolysis in that the products do not consist of free base and free acid. One of the most familiar cases is the decomposition of silver thiosulfate: $\text{Ag}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{Ag}_2\text{S} + \text{H}_2\text{SO}_4$. In organic chemistry, there are many hydrolytic reactions that are not the reverse of neutralization. For example, cane sugar is hydrolyzed into glucose and fructose, thus: $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6$ (glucose) + $\text{C}_6\text{H}_{12}\text{O}_6$ (fructose). These reactions are seldom reversible.

Significance of Neutrality.—The fact that a salt solution is neutral is not evidence of the absence of hydrolysis. Ammonium acetate, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, is considerably hydrolyzed, and yet its solution is neutral. This follows from the fact that the base and acid formed are of equal strength, so that the relative numbers of H^+ and OH^- ions remain unchanged.

Rules for Hydrolysis.—Various sets of rules have been proposed to generalize hydrolytic reactions. One form is shown in Table 14.

TABLE 14.—HYDROLYSIS OF SALTS

Type of Salt	Degree of Hydrolysis
Strong base-strong acid.....	None
Strong base-weak acid.....	Partial
Weak base-strong acid.....	Partial
Weak base-weak acid.....	Considerable
One component very weak.....	Complete

Rules like these hold in most cases. However, there are many exceptions, and these exceptions are so important that certain qualifications are necessary.

The influences favoring hydrolysis of salts are: (1) solubility of the salt in water, (2) high ionization of the dissolved salt, and (3) high stability of one or both of the hydrolytic products owing to (a) low solubility or (b) slight ionization. The rules in the

preceding table take into account only the degree of ionization of the free base and the free acid. •

The so-called "exceptional" cases may be classified as follows.

Salts of High Insolubility.—Ferric phosphate, FePO_4 , is not hydrolyzed, although it is the salt of a very weak base and a weak acid. Its high insolubility prevents hydrolysis. Carborundum, CSi , and clay, $\text{Al}_2(\text{SiO}_3)_3$, are stable for the same reason.

Un-ionized Salts.—Mercuric cyanide, $\text{Hg}(\text{CN})_2$, does not hydrolyze, although it is very soluble in water, and its constituent base and acid are very weak. Really it is the most stable of all the soluble mercuric salts. Here, ionization of the dissolved salt is lacking. Lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, is another soluble salt that escapes hydrolysis on account of low ionization.

Stable Ions.—The surprising stability of certain complex ions formed by the union of ions of weak bases and weak acids is to be explained in the same way as the stability of nonionizing soluble salts. Ferricyanide ions $\text{Fe}(\text{CN})_6^{--}$ are very stable, showing a very slight tendency to hydrolyze as follows: $\text{Fe}(\text{CN})_6^{--} + 6\text{HOH} \rightleftharpoons \text{Fe}(\text{OH})_3 + 6\text{HCN} + 3\text{OH}^-$. Such a hydrolysis would certainly take place if the ion dissociated into Fe^{+++} and CN^- to even a slight degree. The presence of tartrates prevents the hydrolysis of cupric salts, owing to the formation of stable copper tartrate complex ions.

Stability of Chlorides, Cyanides, Etc.—Certain salts show a surprising resistance to hydrolysis. Chlorides, as a rule, are not hydrolyzed so much as nitrates and sulfates. For example, $\text{Hg}(\text{NO}_3)_2$ hydrolyzes more than HgCl_2 , and $\text{Bi}(\text{NO}_3)_3$ more than BiCl_3 . $\text{Sb}(\text{NO}_3)_3$ does not exist, owing to its complete hydrolysis when its formation is attempted. SbCl_3 , on the other hand, is fairly stable. The failure of chlorides to hydrolyze is due to reduced ionization of some kind, possibly the formation of complex ions, *e.g.*, SbCl_4^- .

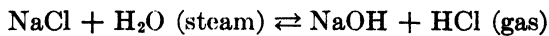
Besides the chlorides, salts of the other halides show a marked resistance to hydrolysis. The same is true of many organic ions, such as cyanide, acetate, oxalate and tartrate. Ferric oxalate, for example, is quite stable.

Effect of Heat on Degree of Hydrolysis.—It has already been seen (page 129) that the dissociation of water into H^+ and OH^- is increased considerably by heat. Since it is the H^+ and OH^-

ions that are responsible for hydrolysis, it follows that increase in temperature should favor hydrolysis in a degree proportional to their concentration. For example, since water is dissociated sixty-two times as much at 100° as at ordinary temperatures, the rate of hydrolysis at the boiling point should be sixty-two times as fast. Furthermore, hydrolytic precipitations that are complete at 100° may be far from complete at room temperature. Soluble $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$ is completely converted into the insoluble basic acetate, $\text{Fe}(\text{OH})_2\text{C}_2\text{H}_3\text{O}_2$, in hot solution, but upon cooling a large amount of the precipitate goes back into solution. This relation may be kept in mind by applying the Le Châtelier principle (page 48) to the equation



Salts of strong bases and strong acids may be hydrolyzed at high temperatures. At least this is indicated by what is known as the Leidenfrost phenomenon. A little solid NaCl is introduced into a red-hot platinum crucible, and about one cubic centimeter of water is slowly introduced. Part of the water is volatilized, forming a cushion of steam which separates the liquid from the hot solids beneath it. After about half a minute, the liquid is poured into a vessel containing blue litmus solution. The red color produced shows that the solution contains HCl . After cooling, the residue in the crucible is dissolved in a little water, and this solution gives a blue color with red litmus, showing that it contains NaOH . The reaction may be represented thus:



Hydrolytic Constant.—The mass law can be applied to incomplete hydrolyses as follows:

Let CA be a salt, forming the cation C^+ and the anion A^- (or C^{++} and A^-), and h be the fraction hydrolyzed, forming the base COH and the acid HA . And let V be the volume of the solution containing 1 mole of CA . V is therefore the reciprocal of concentration.

For the system $\text{CA} + \text{HOH} \rightleftharpoons \text{COH} + \text{HA}$, the mass law expression is

$$\frac{[\text{COH}][\text{HA}]}{[\text{CA}]} = K_{\text{hydrolysis}} \quad (\text{I})$$

The equilibrium constant in this expression is called the *hydrolytic constant* and is usually designated " $K_{\text{hydrolysis}}$." Its value varies with the salt under consideration. The expression as just given does not take into account any ionization of the salt, base, or acid. Allowing for these, the following general cases may be distinguished.

Case I. Salts of Strong Bases and Weak Acids.—Here it may be assumed that the salt CA and the base COH are completely ionized. The equation then takes the form $C^+ + A^- + HOH \rightleftharpoons C^+ + HA + OH^-$. This may be further simplified by dropping C^+ from both sides, leaving $A^- + HOH \rightleftharpoons HA + OH^-$. The amount of A^- in V liters will be $1 - h$ moles, and its concentration will be $(1 - h)/V$. There will be h moles of HA and h gram ions of OH^- , and their concentrations will be h/V in both cases. Substituting the mass law expression for $A^- + HOH \rightleftharpoons HA + OH^-$,

$$K_{\text{hydrolysis}} = \frac{[HA][OH^-]}{[A^-]} = \frac{\frac{h}{V} \cdot \frac{h}{V}}{\frac{1-h}{V}} = \frac{h^2}{V(1-h)} \quad (\text{II})$$

If h is very small, $1 - h$ will be practically unity, and the expression may be written

$$K_{\text{hydrolysis}} = \frac{h^2}{V} \quad (\text{III})$$

Case II. Salts of Weak Bases and Strong Acids.—Assuming, as before, that the strong electrolytes are completely ionized, we have the system $C^+ + HOH \rightleftharpoons COH + H^+$. As before, $[C^+] = (1 - h)/V$, and $[COH]$ and $[H^+] = h/V$. Substituting,

$$K_{\text{hydrolysis}} = \frac{[COH][H^+]}{[C^+]} = \frac{\frac{h}{V} \cdot \frac{h}{V}}{\frac{1-h}{V}} = \frac{h^2}{V(1-h)} \quad (\text{IV})$$

Or, if h is small,

$$K_{\text{hydrolysis}} = \frac{h^2}{V} \quad (\text{V})$$

Case III. Salts of Weak Bases and Weak Acids.—In this case, the salt only may be assumed to be completely ionized. So the equilibrium involved is $C^+ + A^- + HOH \rightleftharpoons COH + HA$. As in the preceding cases, $[C^+]$ and $[A^-] = (1 - h)/V$, and $[COH]$ and $[HA] = h/V$. Substituting,

$$K_{\text{hydrolysis}} = \frac{[COH][HA]}{[C^+][A^-]} = \frac{\frac{h}{V} \cdot \frac{h}{V}}{\left(\frac{1-h}{V}\right)^2} = \frac{h^2}{(1-h)^2} \quad (\text{VI})$$

Since hydrolysis is considerable in this case, it may not be permissible to assume that $(1 - h)$ approximates unity. It should be noted that V is absent from the final expression, indicating that, in this case, the degree of hydrolysis is the same for all dilutions.

CALCULATION OF EXTENT OF HYDROLYSIS

The amount of hydrolysis may be calculated from the ionization constants of the molecules involved. The results are only approximate, for it is necessary to assume that the process can be reduced to a single major reaction. For example, strong electrolytes are assumed to be completely ionized, and weak electrolytes are assumed to be un-ionized. Intermediate products in a hydrolysis are neglected. However, when properly applied, the results obtained fit the experimental facts surprising well.

Again the hydrolysis is classified on the basis of the strength of the base and acid formed.

Case I. Strong Base and Weak Acid.—The type equation is $A^- + \text{HOH} \rightleftharpoons \text{HA} + \text{OH}^-$. Applying the mass law,

$$K_{\text{hydrolysis}} = \frac{[\text{HA}][\text{OH}^-]}{[A^-]} = \frac{[\text{HA}][\text{H}^+][\text{OH}^-]}{[\text{H}^+][A^-]} = \frac{K_{\text{H}_2\text{O}}}{K_{\text{acid}}} \quad (\text{VII})$$

On page 136, the hydrolytic constant of a salt of a strong base and weak acid was found to have the value $\frac{h^2}{V(1-h)}$, where h is the fraction hydrolyzed and V is the volume containing 1 mole of the salt. Therefore,

$$\frac{h^2}{V(1-h)} = \frac{K_{\text{H}_2\text{O}}}{K_{\text{acid}}} \quad (\text{VIII})$$

If inspection shows h to be negligibly small, the equation may take the simpler form

$$h = \sqrt{\frac{V \cdot K_{\text{H}_2\text{O}}}{K_{\text{acid}}}} \quad (\text{IX})$$

On the other hand, for very weak acids, where K_{acid} is of the order of 10^{-12} or less, the h in $1 - h$ becomes too large to be neglected, and the original expression must be used.

Example.—Calculate the percentage hydrolysis of 0.1 M KCN. The ionization constant for HCN is 7×10^{-10} ; the ion product of water is 1×10^{-14} . Here V is 10 l.

A. Solution using the original formula (VIII): Substituting in

$$\frac{h^2}{V(1-h)} = \frac{K_{\text{H}_2\text{O}}}{K_{\text{acid}}}$$

we have

$$\begin{aligned}\frac{h^2}{10(1-h)} &= \frac{1 \times 10^{-14}}{7 \times 10^{-10}} \\ h^2 &= (1-h) \frac{10 \times 10^{-14}}{7 \times 10^{-10}} = (1-h) \times 1.4 \times 10^{-4} \\ h^2 &= 0.00014 - 0.00014h \\ h &= 0.011834, \text{ or } 1.1834\%\end{aligned}$$

B. Solution, using simplified formula (IX): Substituting in

$$\begin{aligned}h &= \sqrt{\frac{V \times K_{H_2O}}{K_{acid}}} \\ h &= \sqrt{\frac{10 \times 10^{-14}}{7 \times 10^{-10}}} = \sqrt{\frac{1.4}{10^4}} = \frac{11832}{100} \\ h &= 0.011832, \text{ or } 1.1832\%\end{aligned}$$

It should be noticed that the two methods give practically identical results, thereby justifying the use of the simpler formula.

Case II. *Weak Base and Strong Acid.*—The type equation is $C^+ + HOH \rightleftharpoons COH + H^+$. The treatment is similar to that for Case I.

$$K_{hydrolysis} = \frac{[COH][H^+]}{[A^+]} = \frac{[COH][H^+][OH^-]}{[C^+][OH^-]} = \frac{K_{H_2O}}{K_{base}}$$

Equating this value with the one derived on page 136,

$$\frac{h^2}{V(1-h)} = \frac{K_{H_2O}}{K_{base}} \quad (X)$$

If h in $(1-h)$ is negligible, the expression may be simplified further.

$$h = \sqrt{\frac{V \cdot K_{H_2O}}{K_{base}}} \quad (XI)$$

It should be noted that the degree of hydrolysis in Cases I and II varies directly as the square root of the volume (or dilution).

Case III. *Both Base and Acid Are Weak.*—The type equation is $C^+ + A^- + HOH \rightleftharpoons COH + HA$. Applying the mass law,

$$K_{hydrolysis} = \frac{[COH][HA]}{[C^+][A^-]} = \frac{[COH][HA][H^+][OH^-]}{[C^+][OH^-][H^+][A^-]} = \frac{K_{H_2O}}{K_{base} \cdot K_{acid}}$$

Substituting in the equation for the hydrolytic constant,

$$\frac{h^2}{(1-h)^2} = \frac{K_{H_2O}}{K_{base} K_{acid}}$$

or

$$\frac{h}{1-h} = \sqrt{\frac{K_{H_2O}}{K_{base} K_{acid}}} \quad (XII)$$

If by inspection it can be seen that h is very small (1 per cent, or less), it may be neglected in the denominator of the first term, and the equation will take the simpler form

$$h = \sqrt{\frac{K_{H_2O}}{K_{base}K_{acid}}} \quad (XIII)$$

This expression can be used in calculating hydrolysis for salts where the values of K_{base} and K_{acid} are not too small,—say not less than 10^{-9} . In the case of salts of very weak bases and acids, h is too large for $(1 - h)$ to be approximated to 1.

Note that V does not appear in either of the expressions for Case III. That is, the degree of hydrolysis of salts of weak bases with weak acids is not increased by dilution but is determined wholly by the strength of the base and acid, assuming that the salt is soluble and well ionized.

Example.—Calculate the percentage hydrolysis of 0.15 M NH_4CN . The ionization constants of NH_4OH and HCN are 1.6×10^{-5} and 7×10^{-10} , respectively. The ion product of water is 1×10^{-14} .

A. Solution, using formula (XII): Substituting in

$$\begin{aligned} \frac{h}{1-h} &= \sqrt{\frac{K_{H_2O}}{K_{base}K_{acid}}} \\ \frac{h}{1-h} &= \sqrt{\frac{1 \times 10^{-14}}{1.6 \times 10^{-5} \times 7 \times 10^{-10}}} = \sqrt{\frac{10^{-14}}{1.12 \times 10^{-14}}} \\ \frac{h}{1-h} &= 0.952 \\ h &= 0.48, \text{ or } 48\% \end{aligned}$$

B. Solution, using simplified formula (XIII): Substituting in

$$\begin{aligned} h &= \sqrt{\frac{K_{H_2O}}{K_{base}K_{acid}}} \\ h &= \sqrt{\frac{1 \times 10^{-14}}{1.6 \times 10^{-5} \times 7 \times 10^{-10}}} = 0.952 \\ h &= 0.952, \text{ or } 95.2\% \end{aligned}$$

The result does not agree with that found in Solution A, above. Evidently the ionization constants of the base and acid are too small to permit the use of the approximate formula.

Limitations of Calculations.—Calculations, such as the above, may be applied to cases where the principal reaction is a single step, but not to systems containing intermediate products not appearing in the over-all equation. For example, a calculation cannot be made for the system $CO_3^{--} + 2HOH \rightleftharpoons H_2CO_3 + 2OH^-$, for it does not take into account the HCO_3^- ions, which really constitute 92 per cent of the system. Such problems must

be solved in two steps: *i.e.*, by determining (1) the concentration of HCO_3^- , and from this (2) the concentration of H_2CO_3 . The expression $\text{CO}_3^{--} + 2\text{HOH} \rightleftharpoons \text{H}_2\text{CO}_3 + 2\text{OH}^-$ *does not tell the truth*. The ratio of H_2CO_3 to OH^- is not 1:2; it is nearer 1:5,000.

Representative Hydrolytic Values.—The degree of hydrolysis of the ordinary salts of weak bases and weak acids is much less

TABLE 15.—PERCENTAGE HYDROLYSIS OF REPRESENTATIVE SALTS AT 25°

Salt	Molar solution	0.1 molar solution	0.01 molar solution
$\text{NaC}_2\text{H}_3\text{O}_2$	0.0025 %	0.008 %	0.025 %
NH_4NO_3	0.0025	0.008	0.025
$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	0.625	0.625	0.625
NH_4CN	48	48	48
Na_2CO_3	1.28	4	12
Na_2S	90	99	99.9

than many people suppose. Table 15 shows the percentage hydrolysis at 25° of three concentrations of typical salts.

Exercises

1. What is the H^+ concentration of water at 25°?
2. Calculate the concentration of H^+ on 0.1 *M* NaOH (90 per cent ionized).
3. Calculate the molar concentration of water.
4. Heat increases the electrical conductivity of water markedly. Explain this effect.
5. Why is a solution of NaH_2PO_4 acidic, while Na_2HPO_4 is basic?
6. Calculation of the degree of hydrolysis of Na_2S indicates almost complete hydrolysis. What formulas should be written on the label for a solution of this salt?
7. Show by equations the hydrolytic products, if any, of the following: Cl_2 , $\text{Mn}(\text{NO}_3)_4$, $\text{Cr}_2\text{O}_7^{--}$, Al_2S_3 , Fe_2S_3 , $\text{Ag}_2\text{S}_2\text{O}_3$, $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$, and CrO_3 . Indicate the cases in which the hydrolysis is practically complete, and the case in which heating strongly favors hydrolysis.
8. Name a metal that will vigorously displace H^+ ions from water; a nonmetal that will preferentially combine with the OH^- ion.
9. Calculate the approximate values of the concentrations of (a) CO_3^{--} , (b) HCO_3^- , and (c) OH^- in *M* Na_2CO_3 (100 per cent ionized). K_1 and K_2 for H_2CO_3 are 3×10^{-7} and 6×10^{-11} , respectively.
Ans.: (a) 0.9872 molar, (b) 0.0128 molar, (c) 0.0128 molar.
10. Calculate the ionization constant of a weak acid if a molar solution of its Na^+ -salt is 50 per cent hydrolyzed.
Ans.: 4×10^{-14} .

11. What is the value of h in formula (XII), if K_{base} and K_{acid} are each equal to 10^{-7} ?

12. Calculate the fraction of 0.001 M AgNO_2 hydrolyzed, if

$$K_{\text{AgOH}} = 1.1 \times 10^{-4}$$

and $K_{\text{HNO}_2} = 4 \times 10^{-4}$. What difference would it make if the approximate formula (XIII) were used?

13. What must be the relation between K_{acid} and K_{base} for the solution of a salt of a weak base and a weak acid to be acidic? Would you expect it to be strongly acidic in any case? Why?

14. Use formula (XIII) to calculate the degree of hydrolysis of a salt of a strong base and a strong acid, assuming that K for each is 1.

15. What form would formula (XII) take if K_{base} became 1? Would the expression be accurate?

CHAPTER XII

REACTIONS AND EQUATIONS

The terms *reaction* and *equation* are sometimes used almost synonymously by people who should know better. It is no wonder that students are sometimes heard to use such expressions as "write the reaction" or even "describe the equation."

A *reaction* is the phenomenon produced in a chemical change, e.g., the formation of a precipitate, a change in color, or the liberation of heat. An *equation*, on the other hand, is a piece of algebraic shorthand used to show the relative amounts of the reactants and the products in the reaction. It differs from ordinary mathematical equations in one respect, viz.: The test for the correctness of a mathematical equation is the equivalence of the two sides; a chemical equation, however, in addition to equivalence, must be a statement of *fact*. Mere "balancing" does not make an expression a chemical equation. To illustrate: The expression $\text{CuS} + 2\text{HNO}_3 = \text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{S}$ is perfect as a specimen of the mathematician's art but absolutely false as a statement of chemical behavior. H_2S cannot be formed in a solution containing free HNO_3 .

It is the purpose of this chapter to withdraw excess emphasis from the balancing of equations and to direct attention to the more important issue—what are the products involved? Knowing the products is chemistry; balancing the equation is a mathematical "stunt."

What Are the Products in a Reaction?—This question can be settled only by actual experiment, best by the student himself. When a student studies a reaction experimentally, he will probably remember the products; if he copies an equation from a textbook or a notebook, he will, with equal probability, forget it. This is the excellence of the laboratory method for studying the sciences.

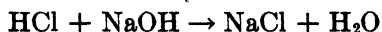
In most cases, the products of a reaction may be recognized by their conspicuous properties; in some cases, simple qualitative

tests may be necessary. For example, when zinc dissolves in concentrated sulfuric acid, the gaseous product will not burn but has the odor of burnt sulfur; therefore it is sulfur dioxide and not hydrogen. Again, a metallic sulfide reacts with dilute nitric acid with the evolution of a gas that turns brown upon mixing with the air. This gas is evidently nitric oxide and not hydrogen sulfide. Mistakes in products in laboratory experiments are usually due to the student's failure to make any attempt to study and identify reaction products.

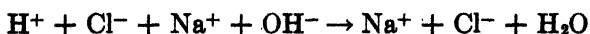
Sometimes the products of a reaction have no conspicuous properties; for example, they are left as ions in the solution. Such products may generally be detected by simple qualitative tests. For example, an iodine solution is bleached by means of a sulfite solution. Simple tests show that the iodine has been changed to the iodide ion, and the sulfite radical to sulfate, SO_4^{--} . It should be admitted that, in some cases, products are hard to identify; *e.g.*, I_2 solutions change thiosulfate, $\text{S}_2\text{O}_3^{--}$, into tetrathionate, $\text{S}_4\text{O}_6^{--}$. In cases like this, it is proper that the student should get help from his instructor or from the text or other reference books. But such cases are infrequent.

With increasing experience in laboratory work, the student will find that there are certain fundamental principles operating in reactions, and from these he may predict the products in most reactions with considerable confidence. Every ion or molecule has a more or less specific chemical behavior which should be learned thoroughly. The student will then be able to interpret reactions and even make them obey his will, so as to bring about separations and special tests.

Ionic Equations.—Until recently, the equations of inorganic chemistry have represented the reactions as between molecules. For example, the neutralization of hydrochloric acid by sodium hydroxide was written



But is this a statement of fact? It is now well established that hydrochloric acid, sodium hydroxide, and sodium chloride are present in solutions as ions and not as molecules. It follows then that, if the equation is to tell the truth, it must be written

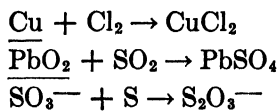


The Na^+ and Cl^- , it appears, undergo no change, and so the equation is simplified to $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$. The student who has been taught to write equations in the molecular form will find the change to ionic equations difficult at first, but in the end ionic equations will be found much simpler.

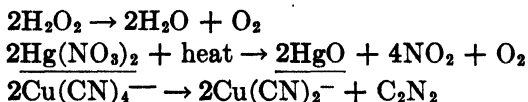
The accepted convention for ionic equations is to represent strong electrolytes as ions and weak electrolytes as molecules. This is not meant to imply that all the activity of strong electrolytes is inherent in the ions and that of the weak electrolytes in the molecules. The convention simply represents each substance in its principal form. The question as to how much the molecules may enter into a reaction is a difficult one and will be discussed later.

Types of Reactions.—The more important types of reactions, with illustrative equations, are given below.

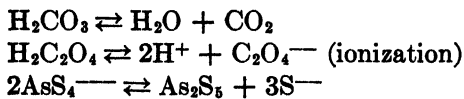
1. *Combination.*—The union of two or more substances (molecules or ions), forming a new compound; *e.g.*,



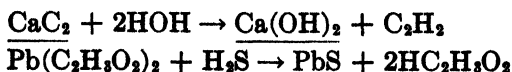
2. *Decomposition.*—The breaking down of a compound into simpler substances; *e.g.*,



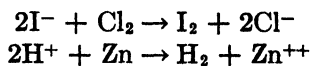
3. *Dissociation.*—Reversible decomposition; *e.g.*,



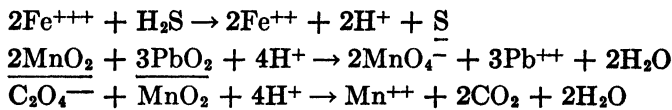
4. *Metathesis.*—An exchange of radical or ions between two substances; *e.g.*,



5. *Displacement*.¹—The substitution of a radical or ion by a more active substance; *e.g.*,



6. *Oxidation-reduction*.—Reactions in which two or more elements change valences; *e.g.*,



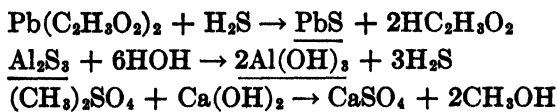
These reactions sometimes appear very complex, owing to the superposing of other types of reactions.

The first three of the types listed in the preceding paragraphs are quite simple, and presumably no discussion is needed. The last three sometimes give trouble and are therefore given somewhat extended treatment.

METATHESIS

Previous to the ionic theory, reactions between electrolytes were considered “a swapping of partners” or, in a more learned vein, metathesis. To illustrate: The reaction between solutions of silver nitrate and hydrochloric acid was represented thus: $\text{AgNO}_3 + \text{HCl} = \text{AgCl} + \text{HNO}_3$. It is now generally accepted that the nitric acid is present mainly, if not wholly, in the form of ions. So the reaction may be more simply represented as combination: $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$. But the term *metathesis* is so impressive and awe-inspiring that it probably will be retained for those reactions between electrolytes where no oxidation or reduction is involved.

There are a number of reactions between weak electrolytes that are truly metathetical in form when represented by equations, *e.g.*,

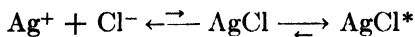


¹ Strictly speaking, displacement is a simple form of oxidation-reduction.

Perhaps reactions in nonionizing solvents should also be included.

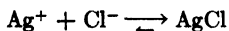
There are certain influences that strongly favor the forward reaction in metatheses, *viz.*: precipitation, volatilization, and formation of stable complexes.

1. Precipitation.—It is easily understood that a reaction will be favored if one of the products is insoluble. As fast as molecules of the insoluble product are formed, they are removed from the equilibrium by precipitation, thereby preventing any backward reaction (*i.e.*, ionization). For example:



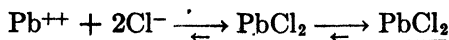
The ionization of AgCl is limited by its insolubility. Presumably AgCl would give high concentrations of Ag^+ and Cl^- if it were only more soluble; *i.e.*, it would be a strong electrolyte. On the other hand, the solution pressure of solid AgCl is very small in comparison with the osmotic pressure of the dissolved AgCl, and this is the determining influence in the system. As a result of these unequal tendencies, the components of the equilibrium are soon tied up in the form of a precipitate.

The complete ionist considers the ions in direct equilibrium with the solid, without any intervention of dissolved AgCl molecules, thus:



Whether the formation of ions is direct or stepwise is of no consequence when it comes to considering the over-all effect. There are so many cases where the dissolved solute cannot be considered completely ionized that all cases are treated alike.

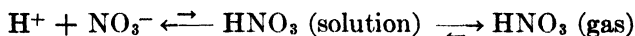
In the above case, the displacement in the equilibrium was due wholly to insolubility. In other cases, repression of ionization may be involved (see common-ion effect, page 85). For example, the solubility of PbCl_2 is reduced by the excess of Cl^- ions.



* In this and similar cases, the relative lengths of the arrows are intended to represent the general trends of the various subreactions, and not the speeds of reactions, which is the usual convention. In every equilibrium, the opposing speeds must be equal.

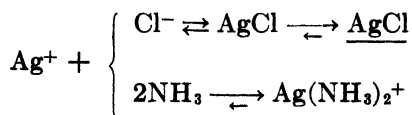
Here the high concentration of Cl^- favors the combination reaction, with a corresponding increase in the amount of the PbCl_2 precipitate. Note the long arrow representing the combination reaction.

2. Volatilization.—In an analogous way, equilibrium will be displaced by volatility. If a solution containing H^+ and NO_3^- ions is heated to a sufficiently high temperature, the HNO_3 formed will begin to escape as a gas. This reaction may be represented thus:



The concentration of the dissolved HNO_3 is small at all times. But as the temperature rises, the vapor pressure of the dissolved HNO_3 becomes greater and greater, until the speed of evaporation is considerable. Eventually the supply of either H^+ or NO_3^- will be used up. The loss of HNO_3 by volatilization, it appears, would not be expected to be rapid.

3. Formation of Complexes of Low Ionization.—Sometimes highly insoluble precipitates dissolve in certain reagents. For example, AgCl dissolves readily in NH_3 solutions. Evidently there is in operation here a directional influence that is superior to insolubility, *viz.*, the formation of a complex of low ionization. Representing the various influences operating in the solution by arrows of graduated length, we have



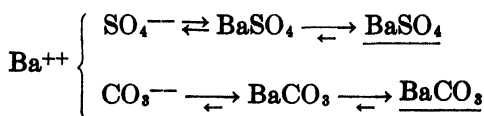
Here the lowest trend of reaction is the dissociation of the complex ion $\text{Ag}(\text{NH}_3)_2^+$ into Ag^+ and NH_3 . That is, $\text{Ag}(\text{NH}_3)_2^+$ sends into solution fewer Ag^+ ions than the insoluble AgCl .

A number of reactions sometimes attributed to volatility are really due to the formation of compounds of low ionization. The volatility of H_2S has a negligible effect on the solubility of FeS in HCl . FeS will dissolve almost as well under pressure, where the H_2S must remain dissolved in the solution, as in an open dish. The decisive influence is the low ionization of H_2S , a very weak

electrolyte. There are rather few cases where the course of a reaction is determined by the formation of a volatile product.

It may now be seen that all three influences—precipitation, volatilization, and formation of complexes of low ionization—may be reduced to the last one. Precipitation displaces equilibrium, since the insolubility of the compound limits its ability to ionize. In exactly the same way, a volatile substance passes into the gaseous state, because that is more stable (*i.e.*, less ionized).

Mass Effects.—The statement, sometimes heard, that reactions proceed in such a direction as to form the compound least soluble under the prevailing conditions is a half-truth, at best. BaSO_4 may be converted into BaCO_3 by an excess of Na_2CO_3 solution, though BaSO_4 is the more insoluble of the two. Presumably, their solution pressures are not altered, and that of BaCO_3 is about nine times that of BaSO_4 . The reaction is due to a mass effect of the CO_3^{--} ion. In the competition between CO_3^{--} and SO_4^{--} ions for Ba^{++} , BaCO_3 molecules are formed more rapidly than BaSO_4 molecules, owing to the high concentration of the CO_3^{--} . As a result, the solubility product of BaCO_3 is exceeded, while that of BaSO_4 is not. Following the removal of Ba^{++} to form BaCO_3 , BaSO_4 dissolves in an attempt to keep the solution saturated with BaSO_4 . The equilibria may be diagrammed as follows:



Note that the arrow representing the solution pressure of BaCO_3 is longer than the solution-pressure arrow of BaSO_4 , but this difference is not sufficient to overcome the effect of the rapid combination of Ba^{++} and CO_3^{--} (long arrow).

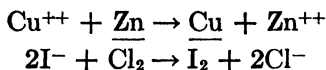
Relative Stability.—The order of the relative stabilities of the various compounds and ions of an element may be roughly determined by appropriate reactions.

To illustrate: Saturated PbCl_2 is less ionized (more stable) than $\text{Pb}(\text{NO}_3)_2$ solution, since Cl^- ions precipitate PbCl_2 from $\text{Pb}(\text{NO}_3)_2$ solution. Saturated PbSO_4 gives a lower concentra-

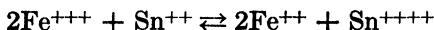
tion of Pb^{++} ions than saturated PbCl_2 , since SO_4^- ions precipitate PbSO_4 from PbCl_2 solution. PbSO_4 is soluble in acetate solutions, indicating that soluble $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ is less ionized than slightly soluble PbSO_4 . CrO_4^- ions precipitate PbCrO_4 from $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution, showing still further reduction of the concentration of the Pb^{++} concentration. PbCrO_4 is soluble in alkali hydroxides, forming plumbite ions HPbO_2^- ; and H_2S will precipitate PbS from plumbite solutions. So these compounds may be arranged in the order of their diminishing Pb^{++} ion concentration as follows: $\text{Pb}(\text{NO}_3)_2 > \text{PbCl}_2 > \text{PbSO}_4 > \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 > \text{PbCrO}_4 > \text{HPbO}_2^- > \text{PbS}$.

DISPLACEMENT

Displacement involves the transfer of electric charges from an ion to an element; *e.g.*,



This definition applies equally well to a certain type of oxidation-reduction reactions, where the charges are transferred from ion to ion; *e.g.*,



Both forms of reactions will be considered together since the theoretical treatment is the same.

The best approach is to consider displacement as consisting of two-part reactions—the ionization of one element and the deionization of another. If a metal is placed in a solution of one of its salts, two actions tend to take place: (1) the formation of ions, more or less held in check by any electric charge on the metal; and (2) the discharge of ions, which depends both on the charge on the metal and the concentration of the ions in the solution. The tendency to send ions into solution is called the *electrolytic solution pressure*; the tendency to discharge ions is simply their *osmotic pressure*. If the electrolytic solution pressure is greater than the osmotic pressure, more ions will be formed than discharged, and the metal will take on a negative charge; if the osmotic pressure is the greater, more ions will be discharged than formed, and the metal will take on a positive charge. The

magnitude of the charge on the metal depends on two things: (1) the metal involved and (2) the concentration of the ions. In order then to compare the electrolytic solution pressures of different metals, it is necessary to select some definite concentration of the ion as a reference point. This is usually the normal (equivalent weight) concentration, but molar concentrations are also used. Electrolytic pressures are measured in volts. For example, a piece of copper in M Cu^{++} ions must be charged with $+0.34$ volt to prevent the discharge of Cu^{++} ions upon it; and zinc in M Zn^{++} ions must have a charge of -0.76 volt to prevent its sending Zn^{++} ions into solution. These charges assumed by metals when placed in contact with molar ionic solutions are called their *molar electrode potentials* and are listed in Table 16. The sign given to these potentials is the sign of the charge on the metal. This list is generally known as the *electromotive* (or *e.m.f.*) *series*.

In many textbooks, the signs of the electrode potentials are the reverse of those given in Table 16. Physical chemists, in particular, like to think of the electrode potential as the tendency to form ions, and consequently the most active metals should have the highest potentials. Physicists and engineers, on the other hand, think that the electrode potential should be the potential of the electrode and favor the signs as given in the table. Without

TABLE 16.—SOME IMPORTANT CATHODIC POTENTIALS (ELECTROMOTIVE SERIES) AT 25°

Electrode	Volts	Electrode	Volts
$\text{K} \rightleftharpoons \text{K}^+$	-2.92	$\text{Fe} \rightleftharpoons \text{Fe}^{+++}$	-0.04
$\text{Na} \rightleftharpoons \text{Na}^+$	-2.72	$\text{H}_2 \rightleftharpoons 2\text{H}^+$	0.00
$\text{Ba} \rightleftharpoons \text{Ba}^{++}$	-2.82(?)	$\text{Sn} \rightleftharpoons \text{Sn}^{++++}$	+0.05
$\text{Sr} \rightleftharpoons \text{Sr}^{++}$	-2.71(?)	$\text{Sn}^{++} \rightleftharpoons \text{Sn}^{++++}$	+0.19
$\text{Ca} \rightleftharpoons \text{Ca}^{++}$	-2.5(?)	$\text{Cu} \rightleftharpoons \text{Cu}^{++}$	+0.34
$\text{Mg} \rightleftharpoons \text{Mg}^{++}$	-2.40(?)	$\text{Fe}^{++} \rightleftharpoons \text{Fe}^{+++}$	+0.40
$\text{Al} \rightleftharpoons \text{Al}^{+++}$	-1.7(?)	$\text{As} \rightleftharpoons \text{As}^{+++}$	(?)
$\text{Zn} \rightleftharpoons \text{Zn}^{++}$	-0.76	$\text{Bi} \rightleftharpoons \text{Bi}^{+++}$	(?)
$\text{Fe} \rightleftharpoons \text{Fe}^{++}$	-0.44	$\text{Sb} \rightleftharpoons \text{Sb}^{+++}$	(?)
$\text{Cd} \rightleftharpoons \text{Cd}^{++}$	-0.40	$\text{Hg} \rightleftharpoons \text{Hg}_2^{++}$	+0.75
$\text{Co} \rightleftharpoons \text{Co}^{++}$	-0.29	$\text{Hg} \rightleftharpoons \text{Hg}^{++}$	+0.80
$\text{Ni} \rightleftharpoons \text{Ni}^{++}$	-0.23	$\text{Ag} \rightleftharpoons \text{Ag}^+$	+0.80
$\text{Sn} \rightleftharpoons \text{Sn}^{++}$	-0.14	$\text{Pt} \rightleftharpoons \text{Pt}^{+++}$	+0.86
$\text{Pb} \rightleftharpoons \text{Pb}^{++}$	-0.13	$\text{Au} \rightleftharpoons \text{Au}^{+++}$	+1.36

doubt, the convention used by the physical chemist is the most useful in calculations.

The potential value of 0 volt assigned to the $\text{H}_2 \rightleftharpoons \text{H}^+$ electrode is an arbitrary value, chosen for reference use. The absolute value for this potential seems to be about +0.277 volt. If this were accepted as the proper molar potential for the hydrogen electrode, all the values in Table 16 would have to be increased by that amount.

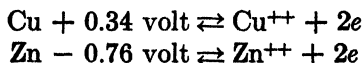
These potentials are calculated for molar concentrations of *ions*, not molecules. The uncertainty of the degree of ionization of the salts of most metals is passed on to the values calculated for the electrode potentials. This explains the differences in the values appearing in different e.m.f. tables.

Displacement Series for the Nonmetals.—Table 17 shows the e.m.f. series for nonmetals. In general, each element will displace from ionic form the elements below it, subject, of course, to concentration effects, as in the case of the metallic elements. Since nonmetals form anions, the residual charge on the electrode will be positive. Therefore the most active element has the largest positive potential. The student is referred to textbooks on physicoelectric chemistry for the methods used in measuring electrode potentials for gases and liquids.

TABLE 17.—ELECTRODE POTENTIALS FOR NONMETALS

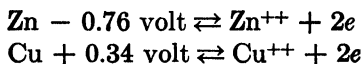
Electrode Reaction	Volts
$\text{F}_2 \rightleftharpoons 2\text{F}^-$	+1.96(?)
$\text{Cl}_2 \rightleftharpoons 2\text{Cl}^-$	+1.36
$\text{O}_2 + 4\text{H}^+ \rightleftharpoons 2\text{H}_2\text{O}$	+1.23
$\text{Br}_2 \rightleftharpoons 2\text{Br}^-$	+1.07
$\text{I}_2 \rightleftharpoons 2\text{I}^-$	+0.54
$\text{S} \rightleftharpoons \text{S}^{--}$	(?)
$\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{OH}^-$	+0.40

The Electrode Reaction.—Since equilibrium in electrode reactions is determined not only by the metal and the concentration of its cation, but also by the charge on the metal, all of these should appear in the equation; *e.g.*,



Following the convention of the signs used in Table 16, the electrode potential is to be regarded as the voltage necessary to maintain a molar concentration of cations in the solution. It

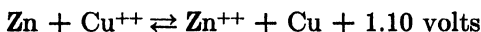
is therefore placed on the left-hand side of the equation with the metal. By combining the equations for electrode reactions so as to eliminate the electrons involved, the energy equations for various displacement reactions (*e.g.*, galvanic cells) may be obtained. For example,



Subtracting,

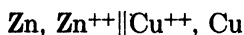


Transposing,



It must be pointed out that 1.10 volts is correct only when $[\text{Cu}^{++}]$ equals $[\text{Zn}^{++}]$. As the reaction proceeds, $[\text{Cu}^{++}]$ decreases and $[\text{Zn}^{++}]$ increases, with a consequent diminution in the voltage—just as would be expected from the Le Châtelier principle (page 48).

Representation of Electric Cells.—Electric cells are represented by enumerating the materials involved, always arranging them in the order that will call for the electronic (negative) current to pass from right to left. For example, the gravity cell is represented thus:



In other words, the anode is placed to the left (*i.e.*, written first). The double bar “||” denotes the separation of two solutions in such a way as to nullify any difference of potentials.

Effect of Concentration on Electrode Potential.—It has already been stated that the potential on a metallic electrode increases with the concentration of the ion in the solution. This relation is represented by the Nernst formula,

$$E = E_0 + \frac{RT}{nF} \ln [\text{ion}]$$

in which E_0 is the molar electrode potential, R is the gas constant (8.315 joules), T is the absolute temperature, n is the valence of the ion, F is the faraday (96,500 coulombs), and \ln denotes the

"natural" instead of the ordinary, or Briggsian, logarithm. This expression may be simplified by substituting for certain of these values and by introducing the constant 2.3 to change the natural logarithm into ordinary form.

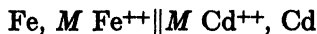
$$E = E_0 + \frac{8.315 \times (273^\circ + 25^\circ)}{n \times 96,500} \times 2.3 \log [\text{ions}]$$

or

$$E = E_0 + \frac{0.058}{n} \log [\text{ions}]$$

To illustrate for a divalent metal: For a tenfold increase in the concentration of the ion, the potential would increase 0.029 volt. This follows from the fact that the logarithm of 10 is 1, so that the term $\frac{0.058}{n} \log [\text{ions}] = \frac{0.058}{2} \times 1$, or 0.029. Similarly a tenfold decrease in the ion concentration would diminish the potential by 0.029 volt, since the logarithm of 0.1 is -1 . For example, the potential of cadmium in M Cd^{++} is -0.400 volt; therefore the potential of the $0.1 M$ Cd electrode is $-0.400 - 0.029$, or -0.429 volt.

Completeness of Displacement.—It is a familiar fact that if any galvanic cell is short-circuited, the voltage will rapidly diminish and finally become 0. At that point all chemical change within the cell ceases. Equilibrium, therefore, is reached only when the potentials of the two electrodes become the same. Applying the mass law to a typical equilibrium $\text{Cu}^{++} + \text{Zn} \rightleftharpoons \text{Cu} + \text{Zn}^{++}$ and recalling that the concentrations of metals are constants, we have $[\text{Zn}^{++}]/[\text{Cu}^{++}] = K$. In this case, $K = 10^{38}$, indicating that the amount of Cu^{++} left in the solution is very small. In the case of metals with a smaller difference in potential, the displacement is less complete. Figure 21 shows the change in potentials for cadmium and iron electrodes in a molar solution of Cd^{++} ions; *i.e.*,



Iron displaces the Cd^{++} ions until the potentials of these two electrodes become the same— -0.441 volt. At this point, Cd^{++} is 0.04 molar, and Fe^{++} is 0.96 molar. Only 96 per cent of the

Cd^{++} has been displaced. If two metals with potentials lying still closer together are tried (*e.g.*, the displacement of Sn^{++} by lead), the reaction will be still less complete. These incomplete displacements are sometimes used in analysis. Metallic lead does not completely reduce Sn^{++++} to Sn^{++} . Rather, an equilibrium mixture is obtained, as follows: $\text{Pb} + \text{Sn}^{++++} \rightleftharpoons \text{Pb}^{++} + \text{Sn}^{++}$. However, the test for Sn^{++} (page 225) is so sensitive that complete reduction is not necessary.

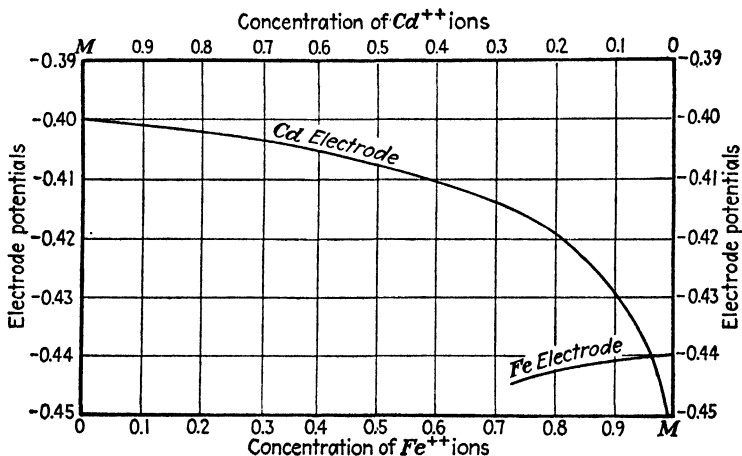
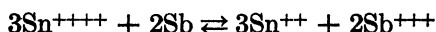


FIG. 22.—Potentials in a cadmium-iron cell.

Elements may show a reducing action on the ions of elements above them in the e.m.f. series. One of the most notable examples of this is the reduction of Sn^{++++} to Sn^{++} by antimony.



Sometimes metals occur in active forms that behave as though they should have a higher place in the e.m.f. series. To illustrate, black mercury will displace silver from AgCl (page 185), and colloidal copper will dissolve rapidly in hydrobromic acid, thus: $\text{Cu} + 2\text{H}^+ \rightarrow \text{Cu}^{++} + \text{H}_2$.

The magnitude of the potential in a displacement reaction is a measure of the vigor or energy of the reaction. The reaction $\text{Zn} + 2\text{H}^+ \rightleftharpoons \text{Zn}^{++} + \text{H}_2 + 0.76$ volt proceeds vigorously; $\text{Sn} + 2\text{H}^+ \rightleftharpoons \text{Sn}^{++} + \text{H}_2 + 0.14$ volt proceeds slowly; and $\text{Cu} +$

$2\text{H}^+ \rightleftharpoons \text{Cu}^{++} + \text{H}_2 - 0.34$ volt does not go at all under ordinary conditions.

Overvoltage.—Electrode reactions are sometimes complicated by a queer irreversibility called *overvoltage*. To illustrate: A voltage higher than the theoretical potential is required to discharge H^+ ions on certain metallic surfaces. Pure zinc, for example, will not directly displace H^+ ions unless the zinc is given an extra negative charge. On the other hand, if the zinc contains impurities with low hydrogen overvoltages, the reaction proceeds readily.

The mechanism of the reaction can be shown by placing a piece of very pure zinc in dilute H_2SO_4 . No reaction occurs. However, if a piece of copper or platinum is brought into contact with the zinc, action starts at once, as shown by the formation of bubbles of hydrogen on the copper or platinum. When contact is broken, the stream of electrons passing from zinc to copper is interrupted, and the action stops. Mercury has a fairly high overvoltage, and zinc electrodes (impure) are amalgamated to keep down "local currents."

A similar effect is found in the excess potential required to discharge OH^- ions on certain surfaces (the "oxygen overvoltage"). This is particularly high with lead and bright platinum.

Representative values for hydrogen and oxygen overvoltages are given in Table 18. The values obtained differ considerably

TABLE 18.—OVERVOLTAGES TOWARD HYDROGEN AND OXYGEN

Hydrogen liberation		Oxygen liberation	
Cathode	Overvoltage	Anode	Overvoltage
Platinum (black).....	0.00	Nickel.....	0.05
Iron.....	0.08	Cobalt.....	0.12
Platinum (bright)....	0.09	Iron.....	0.24
Silver.....	0.15	Platinum (black).....	0.24
Nickel.....	0.21	Lead (PbO_2).....	0.28
Copper.....	0.23	Platinum (bright)....	0.44
Tin.....	0.53		
Lead.....	0.64		
Zinc.....	0.70		
Mercury.....	0.78		

according to the method used and conditions, such as temperature and electrolytes present.

The excess energy required to discharge H^+ and OH^- ions reappears in the form of chemical energy. For example, zinc in the presence of H^+ ions is a much stronger reducing agent than iron, though hydrogen is formed in both cases. Reducing action may be still further intensified by reducing the concentration of the hydrogen ions in the solution. The lower the concentration of H^+ ions, the greater the energy required to discharge them, and the more vigorous is the reducing action. This is illustrated by the fact that zinc is a stronger reducing agent in alkaline than in acid medium.

OXIDATION REDUCTION

In this large group of reactions, the reaction may at first appear to consist of nothing less than a haphazard rearrangement of atoms. Closer examination, however, shows that one or more of the elements undergo increase in valence (oxidation), while others undergo decrease in valence (reduction). Similar changes of valence have been found in displacement, but there the mechanism is too simple to cause trouble. Oxidation-reduction equations, on the other hand, will always remain very perplexing unless the student accepts some theory of the mechanism of such reactions.

In approaching a possible oxidation-reduction reaction, the following questions must be settled: (1) Are the reagents strong enough as oxidizing or reducing agents to react with each other? (2) If a reaction does occur, what reduction products are to be expected from the oxidizing agent, and what oxidation products from the reducing agent? Not until these questions have been properly answered is it permissible to proceed to balancing of the equation.

Oxidation and reduction may be considered from several points of view. An oxidizing agent may be thought of as (1) giving off oxygen (or other negative element), (2) adding hydrogen, and (3) adding electrons. A reducing agent may be thought of as (1) adding oxygen (or other negative element), (2) giving off hydrogen, or (3) giving off electrons. Illustrations of these definitions are:

Oxidizing Agents	Reducing Agents
(1a) $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$	(1a) $2\text{SO}_3^{--} + \text{O}_2 \rightarrow 2\text{SO}_4^{--}$
(1b) $3\text{HCl} + \text{HNO}_3 \rightarrow$ $2\text{H}_2\text{O} + \text{NO} + 3\text{Cl}$	(1b) $2\text{FeCl}_2 + \text{Cl}_2 \rightarrow 2\text{FeCl}_3$
(2) $\text{AsCl}_3 + 6\text{H} \rightarrow \text{AsH}_3 + 3\text{HCl}$	(2) $\text{Mg} + 2\text{HOH} \rightarrow$ $\text{Mg}(\text{OH})_2 + \text{H}_2$
(3) $\text{Fe}^{+++} + e \rightarrow \text{Fe}^{++}$	(3) $\text{Sn}^{++} - 2e \rightarrow \text{Sn}^{++++}$

All these reactions are to be regarded as more or less hypothetical in nature, and not as expressing any ultimate truth. The actual mechanism of oxidation-reduction reactions is not known.

Specific Reactions of Oxidizing and Reducing Agents.—Every oxidizing and every reducing agent has a definite or normal behavior. For example, $\text{Cr}_2\text{O}_7^{--}$ ions are changed by reducing agents to Cr^{+++} , and I^- ions are converted by oxidizing agents to free iodine. In a few cases, the form of the reaction may vary with concentration (*e.g.*, HNO_3), with acidity (*e.g.*, MnO_4^-), or with temperature (*e.g.*, HClO_4). These behaviors are represented by "partial equations" in Table 19. Two types of partial equations are in use, *viz.*: (1) decomposition equations, which represent oxidizing agents as giving off oxygen or other negative element and reducing agents as taking up oxygen or other negative element; and (2) electronic equations, which represent oxidizing agents as gaining electrons and reducing agents as losing electrons. Both types are shown in the table. The behavior of all oxidizing and reducing agents can be represented both ways, but it seems that oxygenation (*i.e.*, addition of oxygen) and deoxygenation (removal of oxygen) are best represented by the decomposition type, while the electronic type is best suited to elements undergoing simple valence changes.

If the student will only take the trouble to learn the preceding partial equations of oxidizing and reducing agents, he will always be able to predict the products formed when they react with each other.

Strength of Oxidizing and Reducing Agents.—It is a very elementary fact that some oxidizing agents are more efficient than others; and conversely, certain reducing agents are more active than others. For example, HNO_3 will not oxidize Mn^{++} at all, HClO_3 will oxidize it to MnO_2 , and $\text{PbO}_2 + \text{H}^+$ will oxidize it to MnO_4^- . Evidently the strengths of these oxidizing agents are in the following order: $\text{HNO}_3 < \text{HClO}_3 < \text{PbO}_2 + \text{H}^+$.

TABLE 19.—SPECIFIC BEHAVIORS OF OXIDIZING AND REDUCING AGENTS
REPRESENTED AS PARTIAL EQUATIONS

<i>Oxidizing Agents (Acidic)</i>	
Decomposition Equations	Electronic Equations ¹
2HNO_3 (dilute) \rightarrow $\text{H}_2\text{O} + 2\text{NO} + [\text{3O}]$	2HNO_3 (dilute) $+ 6\text{H}^+ + 6e \rightarrow 4\text{H}_2\text{O} + 2\text{NO}$
2HNO_3 (conc.) $\rightarrow \text{H}_2\text{O} + 2\text{NO}_2 + [\text{O}]$	2HNO_3 (conc.) $+ 2\text{H}^+ + 2e \rightarrow 2\text{H}_2\text{O} + 2\text{NO}_2$
$2\text{HNO}_3 \rightarrow \text{H}_2\text{O} + 2\text{NO} + [\text{O}]$	$2\text{HNO}_2 + 2\text{H}^+ + 2e \rightarrow 2\text{H}_2\text{O} + 2\text{NO}$
$3\text{HCl} + \text{HNO}_3$ (aqua regia) $\rightarrow 2\text{H}_2\text{O} + \text{NO} + [\text{3Cl}]$	$3\text{HCl} + \text{HNO}_3 + 3e \rightarrow 2\text{H}_2\text{O} + \text{NO} + 3\text{Cl}^-$
H_2SO_4 (hot, conc.) $\rightarrow \text{H}_2\text{O} + \text{SO}_2 + [\text{O}]$	Cl_2 (in H_2O) $+ 2e \rightarrow 2\text{Cl}^-$
$\left\{ \begin{array}{l} \text{HClO}_3 \rightarrow \text{HCl} + [\text{3O}] \\ 3\text{HClO}_3 \rightarrow \text{HClO}_4 + 2\text{ClO}_2 + \text{H}_2\text{O} \end{array} \right.$	Br_2 (in H_2O) $+ 2e \rightarrow 2\text{Br}^-$
$\left\{ \begin{array}{l} \text{HClO}_4 \rightarrow \text{HCl} + [\text{4O}] \\ 2\text{HClO}_4 \rightarrow \text{H}_2\text{O} + [\text{2Cl}] + [\text{7O}] \end{array} \right.$	$\text{Fe}^{+++} + e \rightarrow \text{Fe}^{++}$
$2\text{HMnO}_4 + 4\text{H}^+ \rightarrow 2\text{Mn}^{++} + 3\text{H}_2\text{O} + [\text{5O}]$	$2\text{Hg}^{++} + 2e \rightarrow \text{Hg}_2^{++}$
$\text{H}_2\text{Cr}_2\text{O}_7 + 6\text{H}^+ \rightarrow 2\text{Cr}^{+++} + 4\text{H}_2\text{O} + [\text{3O}]$	$\text{Hg}_2^{++} + 2e \rightarrow 2\text{Hg}$
$\text{PbO}_2 + 2\text{H}^+ \rightarrow \text{Pb}^{++} + \text{H}_2\text{O} + [\text{O}]$	$\text{Ag}^+ + e \rightarrow \text{Ag}$
$\text{MnO}_2 + 2\text{H}^+ \rightarrow \text{Mn}^{++} + \text{H}_2\text{O} + [\text{O}]$	$\text{Fe}(\text{CN})_6^{---} + e \rightarrow \text{Fe}(\text{CN})_6^{----}$
<i>Oxidizing Agents (Alkaline)</i>	
$\text{Na}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 2\text{OH}^- + [\text{O}]$	$\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} + 2e \rightarrow 2\text{Na}^+ + 4\text{OH}^-$
H_2O_2 (in OH^- solution) $\rightarrow \text{H}_2\text{O} + [\text{O}]$	$\text{H}_2\text{O}_2 + 2e \rightarrow 2\text{OH}^-$
$2\text{MnO}_4^- + \text{H}_2\text{O} \rightarrow 2\text{MnO}_2 + 2\text{OH}^- + [\text{3O}]$	$2\text{MnO}_4^- + 4\text{H}_2\text{O} + 6e \rightarrow 2\text{MnO}_2 + 8\text{OH}^-$
OCl^- (Cl_2 in OH^- solution) $\rightarrow \text{Cl}^- + [\text{O}]$	$\text{OCl}^- + \text{H}_2\text{O} + 2e \rightarrow \text{Cl}^- + 2\text{OH}^-$
OBr^- (Br_2 in OH^- solution) $\rightarrow \text{Br}^- + [\text{O}]$	$\text{OBr}^- + \text{H}_2\text{O} + 2e \rightarrow \text{Br}^- + 2\text{OH}^-$
<i>Reducing Agents (Acidic)</i>	
$\text{H}_2\text{S} + [\text{O}] \rightarrow \text{H}_2\text{O} + \text{S}$	$2\text{I}^- \rightarrow \text{I}_2 + 2e$
$\text{H}_2\text{O}_2 + [\text{O}] \rightarrow \text{H}_2\text{O} + \text{O}_2$	$2\text{S}_2\text{O}_3^{--} \rightarrow \text{S}_4\text{O}_6^{--} + 2e$
$\text{NO}_2^- + [\text{O}] \rightarrow \text{NO}_3^-$	$\text{Zn} \rightarrow \text{Zn}^{++} + 2e$
$\text{SO}_3^{--} + [\text{O}] \rightarrow \text{SO}_4^{--}$	$\text{Al} \rightarrow \text{Al}^{+++} + 3e$
$\text{H}_2\text{C}_2\text{O}_4 + [\text{O}] \rightarrow \text{H}_2\text{O} + 2\text{CO}_2$	$\text{Sn}^{++} \rightarrow \text{Sn}^{++++} + 2e$
<i>Reducing Agents (Alkaline)</i>	
$\text{HSnO}_2^- + [\text{O}] \rightarrow \text{HSnO}_3^-$	$\text{S}^{--} \rightarrow \text{S} + 2e$
$\text{Zn} + \text{OH}^- + [\text{O}] \rightarrow \text{HZnO}_2^-$	$2\text{I}^- \rightarrow \text{I}_2 + 2e$
$2\text{Al} + 2\text{OH}^- + [\text{3O}] \rightarrow 2\text{AlO}_2 + \text{H}_2\text{O}$	$\text{Zn} + 3\text{OH}^- \rightarrow \text{HZnO}_2^- + \text{H}_2\text{O} + 2e$

¹ Although "e" is in general use as the symbol for electron, \ominus has the advantage of keeping before the eye of the student the fact that it represents a negative charge of electricity. Many students persist in forgetting what e really stands for, especially when it comes to balancing the charges in equations.

Acidic medium		Basic medium	
Partial equation	Poten- tial, volts	Partial equations	Poten- tial, volts
$\text{NaBiO}_3 + 4\text{H}^+ \rightarrow \text{Na}^+ + \text{Bi}^{+++} + 3\text{H}_2\text{O} + [\text{O}]$	+ (?)	$2\text{OCl}^- \rightarrow 2\text{Cl} + [2\text{O}], \text{ or}$	+ (?)
$2\text{Co}(\text{OH})_2 + 4\text{H}^+ \rightarrow 2\text{Co}^{++} + 5\text{H}_2\text{O} + [\text{O}]$	+ (?)	$2\text{OH}^- + \text{Cl}_2 \rightarrow 2\text{Cl}^- + \text{H}_2\text{O} + [\text{O}]$	+ (?)
$\text{PbO}_2 + 2\text{H}^+ \rightarrow \text{Pb}^{++} + \text{H}_2\text{O} + [\text{O}]$	+1.68	$\text{Na}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 2\text{OH}^- + [\text{O}]$	+1.66
$2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 2\text{Mn}^{++} + 3\text{H}_2\text{O} + [5\text{O}]$	+1.664	$2\text{MnO}_4^- + \text{H}_2\text{O} \rightarrow 2\text{MnO}_2 + 2\text{OH}^- + [3\text{O}]$	+1.63
$\text{HClO}_4 (\text{conc.}) \rightarrow \text{H}^+ + \text{Cl}^- + [4\text{O}]$	+ (?)		
$\text{HClO}_3 \rightarrow \text{H}^+ + \text{Cl}^- + [3\text{O}]$	+1.44		
$\text{MnO}_2 + 2\text{H}^+ \rightarrow \text{Mn}^{++} + \text{H}_2\text{O} + [\text{O}]$	+1.33		
$\text{Cr}_2\text{O}_7^{--} + 8\text{H}^+ \rightarrow 2\text{Cr}^{+++} + 4\text{H}_2\text{O} + [3\text{O}]$	+1.274		
$\text{Cl}_2 + 2e \rightarrow 2\text{Cl}^-$	+1.358		
$\text{Br}_2 + 2e \rightarrow 2\text{Br}^-$	+1.065		
$2\text{HNO}_3 (\text{conc.}) \rightarrow \text{H}_2\text{O} + 2\text{NO}_2 + [\text{O}]$	+ (?)		
$2\text{HNO}_3 (\text{dil.}) \rightarrow \text{H}_2\text{O} + 2\text{NO} + [3\text{O}]$	+0.95		
$\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + [\text{O}]$	+0.86		
$\text{Hg}^{++} + 2e \rightarrow \text{Hg}$	+0.80		
$\text{Ag}^+ + e \rightarrow \text{Ag}$	+0.75		
$\text{Fe}^{+++} + e \rightarrow \text{Fe}^{++}$	+0.535		
$\text{I}_2 + 2e \rightarrow 2\text{I}^-$?		
$\text{H}_2\text{SO}_5 + [\text{O}] \rightarrow \text{H}_2\text{SO}_4$	+0.34		
$\text{Cu}^{++} + 2e \rightarrow \text{Cu}$	+0.13		
$\text{Sn}^{++++} + 2e \rightarrow \text{Sn}^{++}$	+0.2		
$\text{Bi}^{+++} + 3e \rightarrow \text{Bi}$	+0.1		
$\text{Sb}^{+++} + 3e \rightarrow \text{Sb}$	± 0		
$2\text{H}^+ + 2e \rightarrow \text{H}_2$	-0.12		
$\text{Pb} \rightarrow \text{Pb}^{++} + 2e$	-0.13		
$\text{Sn} \rightarrow \text{Sn}^{++} + 2e$	-0.22		
$\text{Ni} \rightarrow \text{Ni}^{++} + 2e$	-0.23		
$\text{Co} \rightarrow \text{Co}^{++} + 2e$	-0.40		
$\text{Cd} \rightarrow \text{Cd}^{++} + 2e$	-0.43		
$\text{Fe} \rightarrow \text{Fe}^{++} + 2e$	-0.55		
$\text{H}_2\text{S} + [\text{O}] \rightarrow \text{H}_2\text{O} + \text{S}$	(?)		
$2\text{HI} + [\text{O}] \rightarrow \text{H}_2\text{O} + \text{I}_2$	-0.76		
$\text{Zn} \rightarrow \text{Zn}^{++} + 2e$			
		$\text{Pb} + \text{OH}^- + [\text{O}] \rightarrow \text{HPbO}_2^-$	- (?)
		$\text{HSnO}_3^- + [\text{O}] \rightarrow \text{HSnO}_3^-$	- (?)
		$\text{Sn} + \text{OH}^- + [\text{O}] \rightarrow \text{HSnO}_3^-$	- (?)
		$\text{Zn} + \text{OH}^- + [\text{O}] \rightarrow \text{HZnO}_2^-$	- (?)

← Reducing Strength Oxidizing Strength →

Again, HCl will not reduce H_2SO_4 at all; HBr will reduce it to SO_2 ; and HI will reduce it to S, or even H_2S . So the strengths of these reducing agents are in the following order: $\text{HCl} < \text{HBr} < \text{HI}$.

The strengths of many oxidizing and reducing agents have been measured by electrochemical means, and evaluated as volts (see Table 20). These values are not absolute but are affected by concentration, acidity, alkalinity, temperature, etc. In the case of H_2O_2 , its behavior is actually reversed upon passing from acidic medium to alkaline medium. In acid medium, H_2O_2 is a mild reducing agent; in alkaline medium, it is a strong oxidizing agent. In acid medium, NO_3^- is a fair oxidizing agent; in neutral medium, it loses this oxidizing action. Such differences as these should be learned and kept in mind.

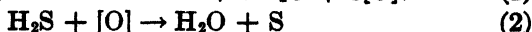
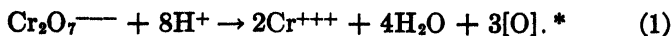
BALANCING EQUATIONS

As insisted above, the most important step in equation building is setting up the proper skeleton of reactants and products. This is a strictly chemical problem, based either on experimental evidence or on the authority of those who have carried out the experiment. Given this skeleton, the next step is to "balance" the sides, so that the statement will conform to the principles of the conservation of matter and of electric charges. Balancing is mainly a mathematical operation.

There are two general methods for balancing oxidation-reduction equations: (1) partial equations and (2) change of valence.

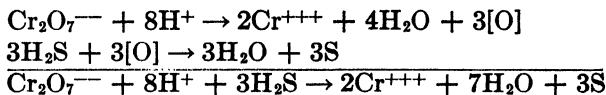
Partial Equations.—In the method of partial equations, the reaction is assumed to consist of two or more steps, each step using up one of the products of another step—a product that does not appear among the final products of the reaction. These partial equations may be of either the decomposition or the electronic types (Table 19). These methods are illustrated in the following paragraphs:

1. *Decomposition Equations.*—Dichromates in acid solution are reduced by H_2S to Cr^{+++} . Referring to Table 19, the partial equations for the oxidizing action of $\text{Cr}_2\text{O}_7^{--}$ and the reducing action of H_2S are

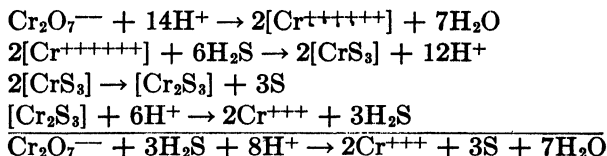


* Brackets are used to denote substances *theoretically*, if not actually, formed.

Since no free oxygen is formed in the experiment, Eq. (2) must be multiplied by 3, so as to use up all the oxygen made available in Eq. (1). Adding these partial equations, with the usual mathematical operation of canceling quantities occurring on opposite sides,

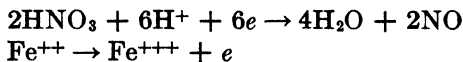


Usually two or more sets of partial equations are possible, differing considerably in detail. For example, the above reaction may be considered to consist of the following partial equations:

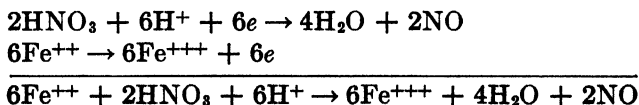


The final equations are the same in both cases, showing that the final expression is independent of the mechanism assumed. However, any proposed mechanism should appear chemically probable.

2. *Electronic Equations.*—The general procedure is similar to the preceding and will be illustrated by the oxidation of Fe^{++} to Fe^{+++} by means of warm dilute HNO_3 . The partial equations for the oxidizing and reducing actions (Table 19) are:

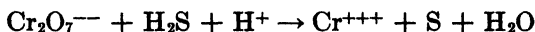


Multiplying Eq. (2) by 6, so as to equate the e term in both equations, and adding,



Change-of-valence Method.—This method is more mathematical than chemical. The principle is that the losses in valence on the part of the oxidizing agents must exactly compensate the gains in valence by the reducing agents. Otherwise the system cannot remain electrically neutral. Electric charges must bal-

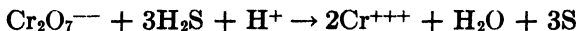
ance as truly as atoms. Illustrating again by the reduction of $\text{Cr}_2\text{O}_7^{--}$ by H_2S , the skeleton equation is



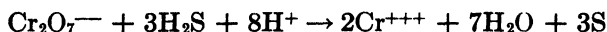
Inspection shows that the valence of the chromium has decreased by 3, and the valence of the sulfur has increased by 2. These losses and gains may be tabulated as follows:

	Losses	Gains
Equating, by multiplying losses by 2	$\text{Cr}^{+6} \rightarrow \text{Cr}^{+3} = 3$	$\text{S}^{-2} \rightarrow \text{S}^0 = 2$
and gains by 3.....	$2\text{Cr}^{+6} \rightarrow 2\text{Cr}^{+3} = 6$	$3\text{S}^{-2} \rightarrow 3\text{S}^0 = 6$

Therefore two atoms of Cr are indicated to every three atoms of S. Hence,



Next, the charges must be balanced. The net charge on the right-hand side is $6+$; so 8H^+ must be used to supply this need. The final reaction then reads



A more difficult equation is the oxidation of As_2S_3 by Na_2O_2 . The skeleton is



The changes in valence are

Losses	Gains
$\text{O}_2^{-2} \rightarrow 2\text{O}^{-2} = 2$	$2\text{As}^{+3} \rightarrow 2\text{As}^{+5} = 4$
	$3\text{S}^{-2} \rightarrow 3\text{S}^{+6} = 24$
	Total 28

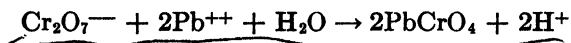
The losses and gains may be equated by taking 14O_2^{-2} radicals to one As_2S_3 .



In order to balance, 16 negative charges are needed on the right-hand side, evidently in the form of 16OH^- . To supply the H and O needed, $8\text{H}_2\text{O}$ must appear on the left-hand side. The final equation, therefore, is

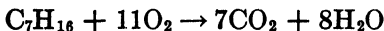


Each of these methods has its advantages. The change-of-valence method is shorter and more timesaving. However, it does not stress the oxidizing and reducing action of the various reactants. Its most serious defect is its limitation to oxidation-reduction reactions; it cannot be applied to metatheses, where there is no change of valence. For example,



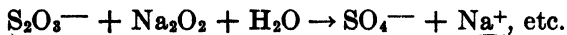
Attempts to apply the change-of-valence method to metathetical equations usually result in errors in the products obtained.

The partial-equations method is longer, and doubtful assumptions have to be made with regard to the intermediate steps. Its advantages are its emphasis on the nature of the reactants and its applicability to all types of reactions. It is particularly serviceable in balancing equations containing organic or other complex molecules. For example, the oxidation of heptane (an important constituent of gasoline) by air is as follows:



This equation is very easy to balance if the reaction is assumed to consist of separate oxidations of C and H. Using the change-of-valence method, on the other hand, absurd assumptions must be made about the valences of the C and H in heptane. If the valence of H is considered +1, the valence of C must be considered $-1\frac{6}{7}$; or if the valence of C is considered +4, the valence of H must be $-\frac{1}{4}$. Organic chemistry teaches that both assumptions are incorrect.

A similar situation is found in the oxidation and reduction of certain inorganic groups. For example,



This would call for a valence of +2 for S, which is assuredly not correct. Probably there are two kinds of sulfur present— S^{+6} and S^{-2} , with an average valence of +2.

These remarks are not intended to confuse the student but to warn him that empirical procedures are merely a means to an end and are not fundamental truths.

Rules for Balancing Equations.—The following rules may be laid down for balancing equations in general:

1. Set up a skeleton equation, listing as products such substances as are indicated by the actual experiment or such as should be expected from the nature of the reactants.

2. Consider the possibilities of the formation of precipitates, gases, or other compounds of low ionization.

3. No acidic substance should appear as a product when an excess of base is present as a reactant. In brief, no product can be formed that is not stable in the presence of excesses of the reacting substances.

4. Note whether oxidizing and reducing agents are present among the reactants. If so and if they are of sufficient strength to react with one another, the normal products of each should appear.

5. Most important of all, the products of a reaction should be determined logically and not by trying to group the atoms together as you would the parts of a puzzle.

6. Excess of atoms left over after an attempt at balancing an equation indicates that the ratio of reactants used is wrong.

7. In ionic equations, electric charges must balance. Balancing charges is as important as balancing atoms.

8. If a substance is well ionized, its formula should be written as its ions; if it is slightly ionized, the molecular formula should be used.

Recapitulation.—In answer to the question as to what determines the course of a reaction, the following principle may be laid down: *Any set of reactants tends to rearrange itself so as to form the set of products that will be most stable under the prevailing conditions of temperature, solubility, etc.* The prime influence in determining this state of maximum stability is minimum ionization. Insolubility and volatility are significant only inasmuch as they are forms of low ionization.

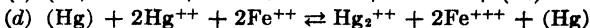
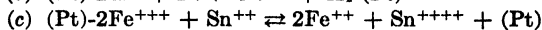
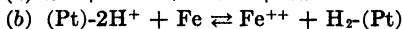
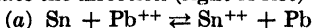
Exercises

1. What metals are insoluble in HNO_3 but soluble in aqua regia?
2. What metals are soluble in NaOH solution? Write equations.
3. Name some compounds for which HCl is a better solvent than HNO_3 . Explain each case.
4. What is the convention for writing equations involving strong and weak electrolytes?
5. Suggest reactions in which the determining influence is (a) precipitate formation, (b) gas formation, (c) formation of stable molecules, (d) formation of stable complex ions.

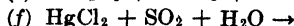
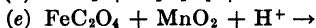
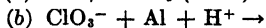
6. Refute with an example the statement that "reactions proceed in the direction that will give the most insoluble compound." (Do not use the $\text{BaSO}_4\text{-Na}_2\text{CO}_3$ reaction.)

7. Calculate the voltage for the reaction $M\text{Fe}^{++} \rightleftharpoons M\text{Fe}^{+++}$.

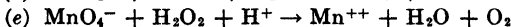
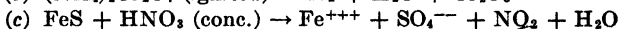
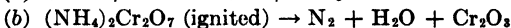
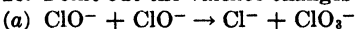
8. Calculate the voltages for molar concentrations in the following cells. State the direction (right or left) of the principal reaction.



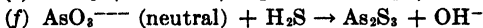
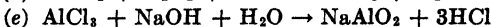
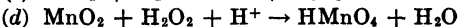
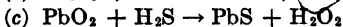
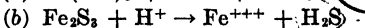
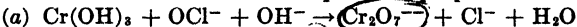
9. Name the products (do not balance) in the following:



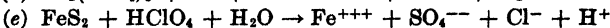
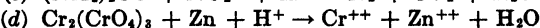
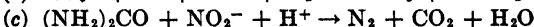
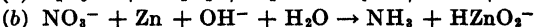
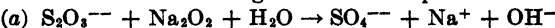
10. Point out the valence changes in the following unbalanced equations:



11. Point out the errors in the products proposed in the following:

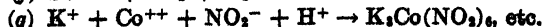
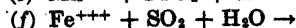
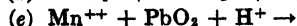
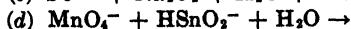
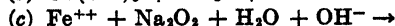
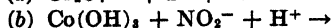
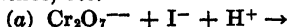


12. Balance the following skeletonized equations:



13. Complete and balance the following oxidation-reduction equations:

Suggestion: First of all, recall the special behaviors of each oxidizing and reducing agent, and derive from these the skeleton of the equation. Then proceed to balance by any suitable method—partial equations, change of valence, etc.



- (h) $\text{Co}^{++} + \text{NH}_4\text{OH} + \text{H}_2\text{O}_2 \rightarrow$
 (i) $\text{Hg}^{++} + \text{HSnO}_2^- + \text{OH}^- \rightarrow$
 (j) $\text{Cr}(\text{OH})_3 + \text{OH}^- + \text{Cl}_2 \rightarrow$
 (k) $\text{MnO}_2 + \text{Fe}^{++} + \text{H}^+ \rightarrow$
 (l) $\text{MnO}_4^- + \text{SO}_2 + \text{H}_2\text{O} \rightarrow$
 (m) $\text{As}_2\text{S}_3 + \text{ClO}_3^- + \text{H}^+ \rightarrow$
 (n) $\text{As}_2\text{S}_3 + \text{H}_2\text{O}_2 + \text{NH}_4\text{OH} \rightarrow$
 (o) $\text{Hg}_2\text{Cl}_2 + \text{dilute } (3\text{HCl} + \text{HNO}_3) \rightarrow$
 (p) $\text{H}_2\text{O}_2 + \text{NO}_2^- \text{ (in alkaline solution)} \rightarrow$
 (q) $\text{HPbO}_3^- + \text{HSnO}_2^- \text{ (in alkaline solution)} \rightarrow$
 (r) $\text{I}^- + \text{PbO}_2 + \text{H}^+ \rightarrow \text{IO}_3^-$, etc.
 (s) $\text{FeS} + \text{HNO}_3 \text{ (hot, dilute)} \rightarrow$
 (t) $\text{K}_2\text{Cr}_2\text{O}_7 \text{ (solid)} + \text{HCl} \text{ (conc.)} \rightarrow$
 (u) $\text{Sn} + \text{HNO}_3 \text{ (very dilute)} \rightarrow \text{NH}_4^+$, etc.
 (v) $\text{Ca}(\text{MnO}_4)_2 \text{ (solid)} + \text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 \text{ (dilute)} \rightarrow$
 (w) $\text{Cu}_2\text{I}_2 \text{ (solid)} + \text{MnO}_4^- + \text{H}^+ \rightarrow$
 (x) $\text{Fe}(\text{CrO}_2)_2 + \text{Na}_2\text{O}_2 + \text{NaOH} \text{ (upon fusion)} \rightarrow$

14. Try to balance the following equations by both the change-in-valence and partial-equations methods:

- (a) $\text{C}_6\text{H}_6 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
 (b) $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{Cr}_2\text{O}_7 + \text{H}^+ \rightarrow \text{C}_2\text{H}_4\text{O} + \text{Cr}^{+++} + \text{H}_2\text{O}$
 (c) $\text{S}_2\text{O}_3^{--} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{--} + 2\text{I}^-$
 (d) $\text{FeS} + \text{HNO}_3 \rightarrow \text{Fe}^{+++} + \text{NO} + \text{S} + \text{H}_2\text{O}$
 (e) $\text{Co}(\text{NO}_2)_6 + \text{H}^+ \rightarrow \text{Co}^{++} + \text{NO}_3^- + \text{NO} + \text{H}_2\text{O}$

Which method do you prefer for involved equations?

15. Point out the error in each of the following equations, and state which of the rules listed on pages 163-164 is violated:

- (a) $\text{Hg}_2\text{Cl}_2 + \text{NH}_3 \text{ (excess)} \rightarrow \text{HgNH}_2\text{Cl} + \text{Hg} + \text{HCl}$
 (b) $\text{PbS} + 2\text{HNO}_3 \rightarrow \text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{S}$
 (c) $\text{HgO} + 2\text{CN}^- + \text{H}_2\text{O} \rightarrow \text{Hg}^{++} + 2\text{CN}^- + 2\text{OH}^-$
 (d) $\text{HgS} + 3\text{HCl} + \text{HNO}_3 \rightarrow \text{HgCl}_2 + 2\text{H}_2\text{O} + \text{NO} + \text{Cl}$
 (e) $\text{MnO}_2 + \text{PbO}_2 \rightarrow \text{MnO}_4^- + \text{Pb}^{++}$
 (f) $\text{Cu}(\text{NH}_3)_4(\text{OH})_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + 4\text{NH}_3 + 2\text{H}_2\text{O}$
 (g) $\text{AlO}_2^- + 3\text{HCl} \rightarrow \text{AlCl}_3 + \text{H}_2\text{O} + \text{OH}^-$
 (h) $2\text{Fe} + 6\text{H}^+ \rightarrow 2\text{Fe}^{+++} + 3\text{H}_2$
 (i) $\text{CuSO}_4 + 6\text{NH}_4\text{OH} \rightarrow \text{Cu}(\text{NH}_3)_4(\text{OH})_2 + (\text{NH}_4)_2\text{SO}_4$
 (j) $2\text{Cr}(\text{OH})_3 + 4\text{H}_2\text{O}_2 (+\text{NH}_4\text{OH}) \rightarrow \text{Cr}_2\text{O}_7^{--} + 7\text{H}_2\text{O}$
 (k) $3\text{PbS} + 8\text{HNO}_3 \rightarrow 3\text{Pb}^{++} + 8\text{NO}_2 + 3\text{SO}_2 + 2\text{H}_2\text{O} + 4\text{H}_2$

PART II
DESCRIPTIVE

CHAPTER XIII

CATION GROUPS—REAGENTS AND SEPARATION

Separation before Identification.—Cations cannot be identified by tests on the original substances. Very few, if any, of the cations have specific tests¹ that may be applied in the presence of cations in general. To illustrate: The SCN^- test for Fe^{+++} is supposed to be highly specific. However, the SCN^- ion forms no red color in the presence of excess Hg^{++} , and it does form a red color in the presence of HNO_3 , even though Fe^{+++} is absent. NaOH may not evolve NH_3 from NH_4^+ in the presence of Hg^{++} . The dimethylglyoxime test for Ni^{++} is possibly the most dependable in the presence of cations in general.

This lack of specific tests calls for some scheme of systematic separation of the cations. They cannot be precipitated one at a time. Even if there were reagents that would remove the cations singly, such a procedure would not be desirable. To separate, say, 25 cations in such a manner would require no less than 24 filtrations on the main solution; and, in view of the losses incurred in filtrations, the tests made on the last ions would probably be weak and indecisive. Furthermore, the excesses of the reagents used in precipitating the earlier cations might "clutter up" the solution to such an extent that satisfactory tests would be almost impossible. Some scheme of precipitating the cations in groups, and later separating the groups into individuals, is far more desirable. Such a procedure has two very important advantages: (1) The number of filtrations on the main solution can be held down to a small number (five or six, at the most) in a complete analysis. (2) If a group is absent, no tests need be made for any of the members of this group. In this way, much time may be saved.

Ideal Groups.—There are certain ideals in planning a system of analysis: (1) The groups should not be too large. Four, or

¹ Some of the new organic reagents used in the drop and spot tests in microanalysis closely approach this ideal specificity (see microanalysis).

perhaps five, is an ideal size. If a group contains too large a number of ions, the precipitate is relatively larger and harder to wash. More than that, the subsequent separation into the component ions is more difficult. (2) The precipitation of each group should be complete. To say the least, not enough of an ion should be carried over to interfere with tests in subsequent groups. (3) The precipitates should form promptly, filter rapidly, and wash well. (4) The precipitates should show little tendency to adsorb or otherwise hold back members of succeeding groups. Unfortunately, none of these ideals can be fully realized.

Group Reagents.—The reagents used in separating a solution into groups are called *group reagents*. Sometimes these reagents are single solutions, but frequently they are mixtures. In the precipitation of cation groups, the anions of the reagent are usually the active portion, though the cations may be important in regulating the concentration of the anions, *e.g.*, H^+ on the ionization of H_2S . Another function of the cations may be the formation of soluble cations, as, for example, NH_4^+ in preventing the precipitation of Mg^{++} . In general, cations may be said to determine the “environment” or tone of a solution. These statements should take on more definite meaning as our study proceeds.

Choice of Group Reagents.—In looking for reagents that will precipitate only a small group of the various cations, we naturally try to think of some anion that forms relatively few insoluble salts. Chloride, bromide, and sulfate are the ones that suggest themselves. The Cl^- ion would precipitate $AgCl$, Hg_2Cl_2 , and $PbCl_2$, though the last one incompletely. The Br^- ion would precipitate Pb^{++} somewhat better, but on the whole it is less desirable than Cl^- and costs more. The SO_4^{--} ion would give precipitates of $BaSO_4$, $SrSO_4$, $CaSO_4$, and $PbSO_4$. The $CaSO_4$ precipitate is by no means complete enough to be satisfactory, and that of $PbSO_4$ and $SrSO_4$ is not ideal. On the whole, the Cl^- ion seems best, since its compounds with H^+ and NH_4^+ are volatile, so that excess Cl^- may be expelled by evaporation. Excess SO_4^{--} is not removed so easily. Furthermore, SO_4^{--} forms some salts of intermediate solubility, such as K_2SO_4 , which might cause trouble by premature precipitation. On the other hand, it must be admitted that the Cl^- ion is not an ideal pre-

cipitant. A special operation must be made in Group II to salvage the Pb^{++} ions not completely precipitated in Group I, in order to prevent interferences with the tests for other ions. Sometimes Pb^{++} is present in so small a quantity that no PbCl_2 is found in Group I, and its detection depends wholly upon results in Group II.

It may seem surprising to the student that analytical procedures are so far from ideal. The present system is admittedly imperfect, but it is the best that chemists have been able to develop in a century of study and laboratory experience.

The Hydrogen Sulfide System.—In separating cations into groups, most texts follow the scheme proposed by Liebig in 1831, in which hydrogen sulfide is the fundamental reagent. Liebig classified cations as follows:

A. Cations precipitated by H_2S in dilute HCl solution: Ag^+ , Hg^{++} , Hg_2^{++} , Pb^{++} , Bi^{+++} , Cu^{++} , Cd^{++} , As^{+++} and As^{++++} , Sb^{+++} and Sb^{++++} , Sn^{++} and Sn^{++++} .

B. Cations not precipitated by H_2S in the presence of dilute HCl , but precipitated by $\text{H}_2\text{S} + \text{NH}_4\text{OH}$: Al^{+++} , Cr^{+++} , Fe^{+++} and Fe^{++} , Zn^{++} , Mn^{++} , Co^{++} and Ni^{++} .

C. Cations not precipitated by H_2S in either HCl or NH_4OH solutions: Ba^{++} , Sr^{++} , Ca^{++} , Mg^{++} , K^+ , Na^+ , and NH_4^+ . In present-day practice, there are two notable modifications of Liebig's scheme: (1) Ag^+ , Hg_2^{++} , and part of the Pb^{++} are precipitated by the HCl used in acidifying the solution. This separation is not necessary, but it is convenient in the detection of Ag^+ and Hg_2^{++} . Group C is subdivided into two groups by means of $(\text{NH}_4)_2\text{CO}_3$.

The table on page 172 shows the cation groups according to the modified H_2S procedure.

Vanadium and tungsten, two elements of increasing industrial importance, are not included. Their chemical behavior is such that they do not fit the general scheme. A number of very rare elements are also omitted.

Objections to Hydrogen Sulfide.—The use of hydrogen sulfide is open to a number of serious indictments:

1. It must be used in the gaseous condition, for it is too insoluble in water for solutions of practicable concentration to be prepared. Furthermore the solution is not very stable.

2. Its precipitating action is slow and apt to be incomplete.
3. Precipitated sulfides are colloidal, filter slowly, and are hard to wash.
4. It is difficult to generate H_2S safely in the amounts required by large groups of students.
5. The presence of the gas in the atmosphere of the laboratory corrodes the metal equipment and frequently spoils other experiments. This fact must be kept in mind.
6. The gas not only has a disagreeable odor but also is poisonous. It is probably as serious a hazard in the laboratory as

TABLE 21.—PERSONNEL OF CATION GROUPS

Group	Reagent	Membership
I	Cl^- (as HCl)	Ag^+ , Hg_2^{++} , Pb^{++} , $[\text{Tl}^+]$
II	H_2S (in presence of dilute HCl)	(a) Hg^{++} , Pb^{++} , Bi^{+++} , Cu^{++} , Cd^{++} (b) As^{+++} , As^{++++} , Sb^{+++} , Sb^{++++} , Sn^{++} , Sn^{++++} , $[\text{Mo}, \text{Au}^{+++}, \text{Pt}^{++++}]$
III	$\text{H}_2\text{S} + \text{NH}_4\text{OH}$ (in the presence of NH_4^+)	(a) Al^{+++} , Cr^{+++} , Zn^{++} , $[\text{U}, \text{rare earths}]$ (b) Mn^{++} , Fe^{++} , Co^{++} , Ni^{++}
IV	CO_3^{--} (as $(\text{NH}_4)_2\text{CO}_3$)	Ba^{++} , Sr^{++} , Ca^{++}
V	No group reagent	Mg^{++} , NH_4^+ , K^+ , Na^+ , $[\text{Li}^+]$

Elements in brackets are rare.

cyanides, though the latter have a worse reputation in the popular mind.

These objections may be met, though not always conveniently. The student must spend more time in making his precipitations and in washing his precipitates. The difficulty of preparing the gas may be obviated by buying the liquefied hydrogen sulfide in steel cylinders in the same way that carbon dioxide is furnished. Students should learn discretion as to the proper use of this gas.

Other Procedures.—Many chemists, in Europe and America, have proposed schemes for analysis without the use of hydrogen sulfide. The fact that these schemes have not been adopted is not due to any lack of progressiveness on the part of the teachers of analytical chemistry. The new procedures have been less accurate and less reliable than the hydrogen sulfide method, and most analysts doubt whether it will ever be possible to replace this gas as the fundamental reagent in qualitative analysis.

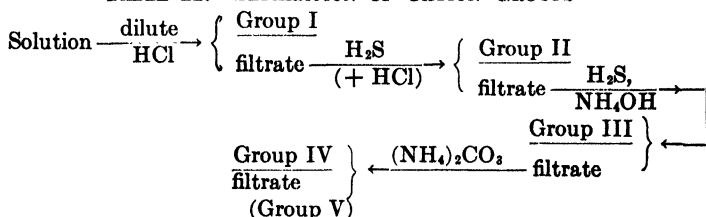
SEPARATION OF CATION GROUPS

The procedures given in different texts differ slightly. Some procedures divide Group III, as given in this book, into two groups, *viz.*: (1) the NH_4OH group, containing Al^{+++} , Cr^{+++} , and Fe^{+++} ; and (2) the $(\text{NH}_4)_2\text{S}$ group, containing Zn^{++} , Mn^{++} , Co^{++} , and Ni^{++} . As the names suggest, the reagents for these groups are NH_4OH (in the presence of NH_4^+) and $\text{NH}_4\text{OH} + \text{H}_2\text{S}$.

Some texts place Mg^{++} in Group IV instead of Group V, as in this book. This is done by precipitating Group IV by $(\text{NH}_4)_2\text{CO}_3$ in the presence of alcohol.

The procedure for the separation of the cation groups is outlined in Table 22.

TABLE 22.—SEPARATION OF CATION GROUPS



Exercises

1. Define *specific test*. Can you give a good example?
2. Who originally proposed H_2S as the fundamental reagent for separating cation groups?
3. Name the reagents for the cation groups. Distinguish between the precipitating ion and the other ions in the reagent.
4. What advantages does Cl^- have over Br^- as a precipitant for Group I?
5. What is the role of the H^+ ion in the reagent for Group I?
6. Why are the tests in the latter cation groups sometimes unsatisfactory?
7. Some textbooks have six cation groups. Explain.
8. Why are precipitated sulfides colloidal?
9. What elements form two cations? In what case are they in different groups?
10. Explain how Mg^{++} can be a member of two groups.

CHAPTER XIV

GROUP I—THE HYDROCHLORIC ACID GROUP

Membership.—Group I contains the cations whose chlorides are insoluble in dilute acids. The membership is as follows:

Lead, Pb^{++}	Mercurous, Hg_2^{++}
Silver, Ag^+	[Thallous, Tl]*

Lead chloride is slightly soluble in cold water (11 g., or 0.04 mole, per liter at 25°), and fairly soluble in hot water. As a result, Pb^{++} ions are not completely precipitated in Group I but appear also in Group II. If Pb^{++} is present in small amount, it may not be found at all in Group I, but wholly in Group II.

Mercury also occurs in both Group I and Group II, but for a quite different reason. Here the dual appearance is due to mercury forming two different cations, *viz.*, mercuric, Hg^{++} , and mercurous, Hg_2^{++} , and only the latter forms an insoluble chloride.

Bismuthyl chloride, BiOCl , and antimonyl chloride, SbOCl , are insoluble in water but soluble in acids. These "oxychlorides" may therefore be carried down in Group I in case the acidity of the solution is too low or in case of high dilution.

Group Reagent.—The reagent used to precipitate Group I is dilute HCl , which furnishes both the Cl^- and the H^+ ions. The Cl^- ion is the actual precipitant, but the H^+ ion is important in keeping Bi^{+++} and Sb^{+++} in solution.

HCl also precipitates from alkaline solution certain insoluble acids and sulfides, *e.g.*, H_2SiO_3 from silicates, H_2WO_4 from tungstates, As_2S_5 from thioarsenates, etc. See Systematic Analysis (page 428) for the procedure to be used in such cases.

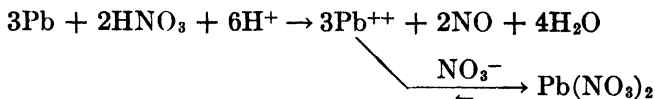
LEAD

The Metal.—Lead is a soft, heavy metal, used industrially in plumbing, telephone cables, storage batteries, and alloys, such as solder, bearing metals, printers' alloys, electric fuses, etc.

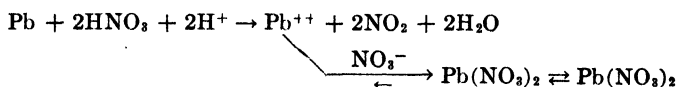
* The thallous ion is not generally included in the scheme of qualitative analysis, owing to the rareness of the element thallium. Cases like this will be indicated in this book by the use of brackets, as above.

Lead compounds are used in paints; storage batteries; insecticides and fungicides; and mordants for calico printing, weighting of silks, and medicines.

The best solvent for metallic lead is dilute HNO_3 , where the water serves as a solvent for the $\text{Pb}(\text{NO}_3)_2$.



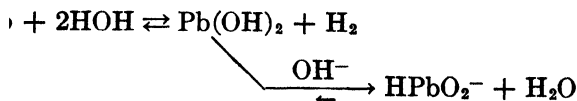
If concentrated HNO_3 is used, crystals of $\text{Pb}(\text{NO}_3)_2$ may form on the surface of the metal and impede the reaction.



Dilute HCl dissolves lead slowly; here again the salt formed interferes by coating the metal. For a similar reason, lead is practically insoluble in dilute H_2SO_4 . When concentrated H_2SO_4 is used, solution is not blocked, since PbSO_4 is soluble in concentrated H_2SO_4 , forming the hydrogen sulfate, $\text{Pb}(\text{HSO}_4)_2$.



Lead is also dissolved slowly by hot alkali solutions, with the liberation of H_2 . Strictly speaking, the lead is dissolved by the water, and the alkali serves to remove the coating of $\text{Pb}(\text{OH})_2$, which would otherwise stop the reaction. The reaction may be diagramed:



The Ion.—Although tetravalent in many compounds, lead forms only one cation, the divalent plumbic (not plumbous) ion Pb^{++} . In alkaline solutions, lead may be present as the plumbate anion HPbO_3^- or the plumbite anion HPbO_2^- . Both of these anions are converted into Pb^{++} cations during the preparation of the solution for cation analysis.

Important Compounds.—The following Pb^{++} compounds are important in the analysis of Group I. A more extensive discussion will be found under Group II (pages 191 to 196).

Lead Nitrate.—This is the most important of the soluble lead salts. It is formed when metallic lead is dissolved in dilute HNO_3 (see page 175).

Lead Chloride.—Lead chloride, PbCl_2 , is a white crystalline salt, formed by the union of Pb^{++} and Cl^- ions. Its solubility

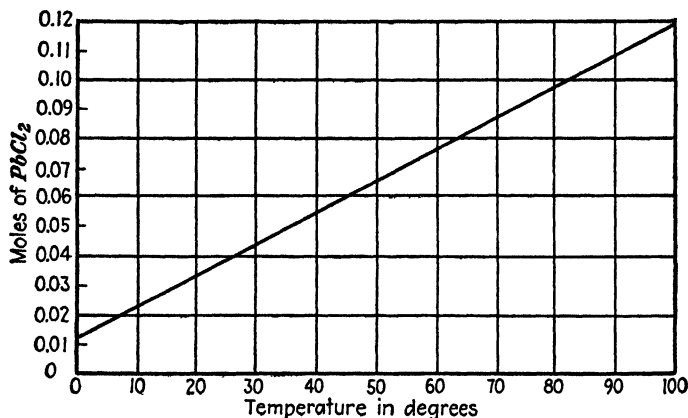
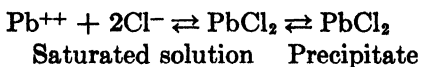


FIG. 23.—Solubility of lead chloride in water.

in water is shown in Fig. 23. It will be noted that the solubility increases rapidly with the temperature, so that it can be said that it is fairly soluble in hot water. Figure 24 shows its solubility at 25° in increasing concentrations of HCl . The solubility decreases from 38.8 millimoles in pure water to 4.4 millimoles in molar HCl . This diminution in solubility is due to the so-called common-ion effect (page 85). This is in accord with the Le Châtelier principle that an increase in the concentration of any factor in an equilibrium drives the reaction in the direction that will absorb this factor. Here the concentration of the Cl^- ion is increased by the addition of HCl .



To use up the excess Cl^- ions, more PbCl_2 molecules must be formed. But, since the solution is already saturated with PbCl_2 ,

its concentration cannot be increased; and so the increase is passed on to the PbCl_2 precipitate. With the equilibrium written as above, it may be said that the equilibrium is "shifted to the right."

Again referring to Fig. 24, it will be seen that beyond M HCl the solubility of PbCl_2 increases rapidly. This is due to the fact that Cl^- ions tend to add themselves to PbCl_2 molecules,

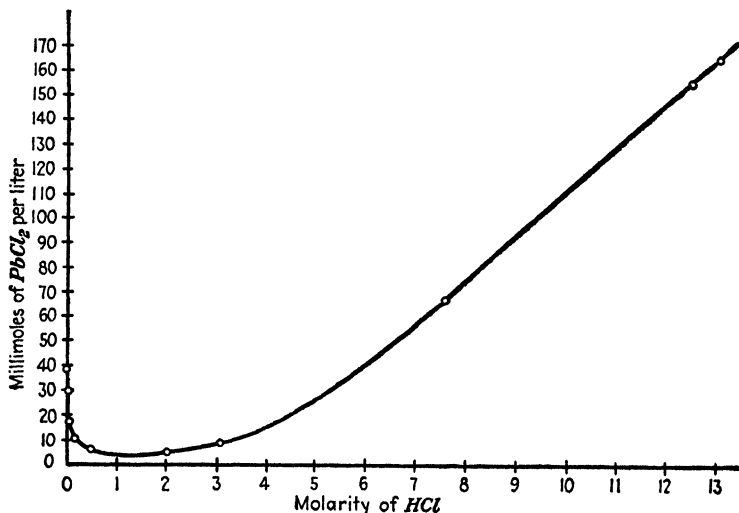
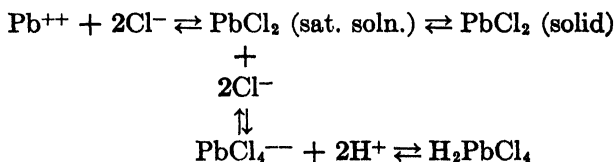


FIG. 24.—Solubility of lead chloride in hydrochloric acid.

forming complex ions—possibly PbCl_4^{--} . These latter ions combine to some extent with the excess of H^+ ions, forming H_2PbCl_4 molecules. The amount of PbCl_2 molecules in the solution would be reduced in this way below the saturation point, and the precipitate dissolves in an attempt to maintain a supply of them. The total equilibrium may be expressed as follows:



Insoluble Lead Compounds.— Pb^{++} ions may be precipitated in a number of forms that may be used as tests for their presence,

e.g., white PbSO_4 , black PbS , and yellow PbCrO_4 . Of these, PbSO_4 is the most soluble and the easiest to overlook. PbS is the most insoluble but the least distinctive; many other sulfides are black and insoluble. PbCrO_4 has in its favor its conspicuous color and its insolubility in acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$. It is therefore used as the confirmatory test.

SILVER

The Metal.—Silver is a white, malleable metal, used industrially in jewelry, coinage, chemical apparatus, dental alloys, etc. It is insoluble in nonoxidizing acids, such as HCl , dilute H_2SO_4 , and dilute HClO_4 . The usual solvent is HNO_3 .



It is also soluble in hot concentrated H_2SO_4 .



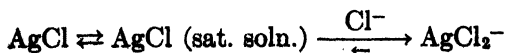
Silver is only slightly attacked by chlorinating agents, such as aqua regia, owing to the separation of insoluble AgCl , which exerts a certain protective action on the metal.

The Ion.—Silver forms the colorless univalent ion Ag^+ . Besides other characteristic reactions, Ag^+ is an oxidizing agent and is reduced by strong reducing agents to metallic silver (usually black).

Analytical Compounds.—Silver forms a number of compounds that are very important in analytical chemistry. The more important of these compounds are discussed in detail below.

Silver Nitrate.—This salt is prepared by dissolving the metal in HNO_3 . It is the most important of the soluble salts.

Silver Chloride.—In analytical procedures, Ag^+ is almost always separated as the chloride. The precipitate darkens upon exposure to light, but this does not affect its analytical properties. AgCl has a very slight solubility in water—0.0015 g., or 0.011 millimole per liter. Furthermore, its solubility in acids is negligibly small. On the other hand, AgCl is readily soluble in NH_3 , NaCN , and $\text{Na}_2\text{S}_2\text{O}_3$ solutions, owing to the formation of complex ions. AgCl dissolves to a considerable extent in large excesses of Cl^- ions, forming a complex anion AgCl_2^- .

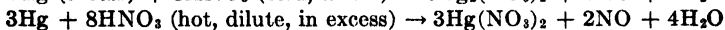
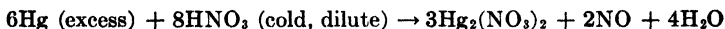


Let us settle the question by calculating the amount of Ag_2S that might be expected from an ordinary filtrate from a Group I precipitation. The volume of this filtrate should not be more than 100 cc., at the most. The concentration of AgCl in water is 1.1×10^{-5} mole per liter, or 1.1×10^{-6} mole per 100 cc. This is equivalent to 0.55×10^{-6} mole of Ag_2S , or 0.000136 g., or 0.136 mg. This amount is too small to be noticed.

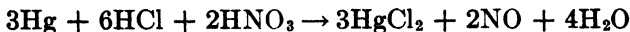
MERCURY

The Metal.—Mercury is a heavy metal, with a silver luster, melting at -39° . It is used in thermometers, barometers, mercury vapor lamps, amalgams, and electrical apparatus. An important use is the extraction of gold and silver from their ores. Its compounds are used in drugs, explosives, etc.

Mercury is insoluble in nonoxidizing acids, such as HCl and dilute H_2SO_4 . It dissolves fairly well in HNO_3 , the products being determined by such conditions as the concentration of the acid, the temperature, and the relative amount of metal and acid. In general, the equations may be written:



It dissolves more readily in aqua regia, forming the slightly ionized HgCl_2 .



The reactions with concentrated H_2SO_4 are slower.

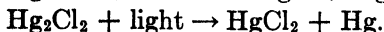
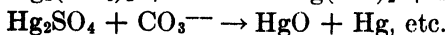
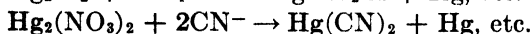
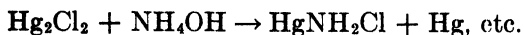


The Ions.—Mercury forms two ions: Hg^{++} (mercuric) and Hg_2^{++} (mercurous). The ions differ in their properties as distinctly as Ag^+ differs from Pb^{++} , or Cu^{++} from Zn^{++} . They belong to different analytical groups. Their only point of contact is that Hg^{++} can be changed into Hg_2^{++} by reduction and Hg_2^{++} into Hg^{++} by oxidation.

MERCUROUS IONS

Constitution of the Mercurous Ion.—The mercurous ion was formerly considered to be univalent, and its formula was written

Hg^+ —*e.g.*, HgCl , HgNO_3 , etc. It was later decided that the ion contains two mercury atoms, and two structures were proposed, *viz.*: —Hg—Hg— , in which both atoms are bivalent; and Hg·Hg^{++} , in which one atom is bivalent and the other of zero valence, being held by its residual valences only. There are two lines of evidence to support this double formula: (1) The density of the vapor of dry mercurous chloride approximates 471. This calls for a formula of Hg_2Cl_2 instead of HgCl , which would correspond to a density of 235.5. (2) Most of the reactions of mercurous compounds indicate that they contain two kinds of mercury. When treated with most reagents, they give a mercuric compound and free mercury. For example:

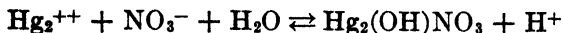


These reactions are best explained by the second formula Hg·Hg^{++} , which, from its structure, would be expected to be unstable. Furthermore, it is hard to see how mercury could separate from a mercurous compound like Cl-Hg-Hg-Cl without disrupting the molecule.

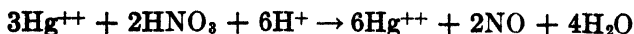
MERCUROUS COMPOUNDS

Only a few mercurous compounds are met in qualitative procedure. The most important are the following.

Mercurous Nitrate.—This is the most important of the soluble mercurous salts. It is partially hydrolyzed by water, giving an insoluble basic nitrate. Hence dilute HNO_3 is used as a solvent. The hydrolysis may be represented:



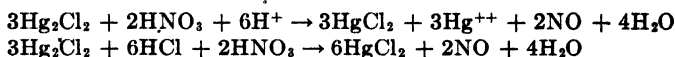
The excess HNO_3 in the solution does not lose its oxidizing power, with the result that, upon standing, $\text{Hg}_2(\text{NO}_3)_2$ solutions may change completely to $\text{Hg}(\text{NO}_3)_2$.



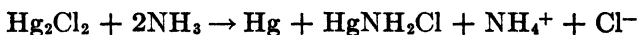
This may be prevented by keeping an excess of metallic mercury in the bottle.

Mercurous Chloride.—The Hg_2^{++} ion unites with Cl^- to form white mercurous chloride (calomel), Hg_2Cl_2 . This has a very low solubility in water—0.00038 g., or 0.0008 millimole, per liter. As in the cases of PbCl_2 and AgCl , when an excess of Cl^- is added, the solubility first falls off and then increases rapidly, presumably owing to the formation of a complex ion, such as $\text{Hg}_2\text{Cl}_4^{--}$.

Mercurous chloride dissolves, upon warming, in HNO_3 and in aqua regia. Note that the product in both cases is a mercuric compound.



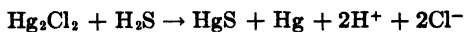
Mercurous chloride is insoluble in ammonia solution but reacts with it to form a mixture of free mercury (as previously mentioned) and an insoluble amino chloride, HgNH_2Cl .



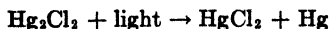
The free mercury is so black that the whole precipitate appears black.

A number of metals when formed from solution are black, although their ordinary forms have other colors, *e.g.*, mercury, platinum, bismuth. Silver is sometimes black, sometimes reddish, sometimes white, depending upon conditions.

Mercurous chloride sometimes darkens when exposed to the atmosphere in the laboratory. This is due to H_2S .

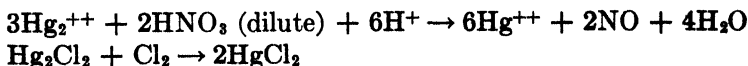


It is also decomposed by strong light.

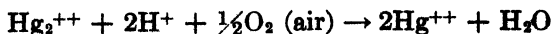


Mercurous Oxide.—When OH^- ions are added to a Hg_2^{++} solution, the precipitate is Hg_2O and not $\text{Hg}_2(\text{OH})_2$. Hg_2O is black and tends to decompose into yellow HgO and free mercury.

Oxidation and Reduction.—Strong oxidizing agents convert mercurous compounds into mercuric compounds. For example:

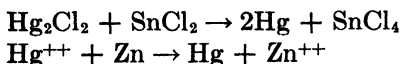


Perhaps the oxygen of the air may assist in this effect.



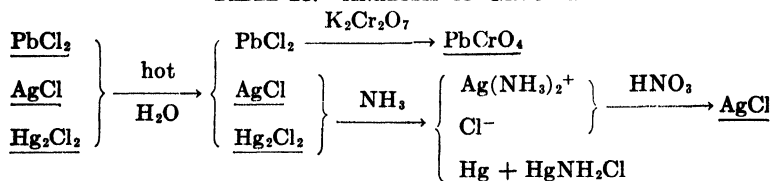
Hence, whenever Hg_2^{++} is detected in Group I, Hg^{++} is to be expected in Group II, unless the solution is freshly prepared or unless it contains free mercury to reduce any Hg^{++} back to the Hg_2^{++} stage: $\text{Hg}^{++} + \text{Hg} \rightarrow \text{Hg}_2^{++}$.

Strong reducing agents, on the other hand, reduce mercurous compounds to free mercury.



Detection.— Hg_2^{++} ions are detected by separating them as white Hg_2Cl_2 and then adding NH_4OH , forming $\text{HgNH}_2\text{Cl} + \text{Hg}$, which appears black.

TABLE 23.—ANALYSIS OF GROUP I



Discussion.—The following theoretical points should be noticed.

Acidification of Solution.—Alkaline solutions may contain certain anions that are decomposed by HCl with the formation of precipitates—*e.g.*, SiO_3^{--} , AsS_4^{--} , S_x^{--} , etc. (see note, page 174). In case the unknown solution is alkaline, it should be acidified with dilute HNO_3 and then filtered, so that the HCl precipitate will consist of Group I chlorides only.

Volumes Prescribed.—The volumes suggested (4 cc. of dilute HCl and 40 cc. of solution) give the proper acidity for the precipitation of Group II in the Group I filtrate.

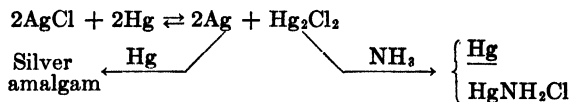
Separation of BiOCl and SbOCl .—The Group I precipitate is washed with dilute HCl to dissolve any bismuthyl chloride, BiOCl , and antimonyl chloride, SbOCl , which may have formed on dilution of the solution to 40 cc.

Basic Lead Chloride.—If the PbCl_2 has not been removed completely by the hot-water treatment, NH_4OH will convert it into white basic lead chloride, $\text{Pb}(\text{OH})\text{Cl}$. This forms a milky suspension which runs through the filter, giving a turbid filtrate. Really this causes no interference with the AgCl test, for $\text{Pb}(\text{OH})\text{Cl}$ is easily soluble in HNO_3 .

Ag^+ in the Presence of Excess Hg_2^{++} .— AgCl cannot be extracted completely by NH_4OH from the black mercury residue. If the Ag^+ is present as a trace only, it may be found wholly in this residue. So if the test for AgCl is negative, Ag^+ may still be found by dissolving the black residue in aqua regia. Upon dilution, the Ag^+ will be left behind as AgCl , which may be filtered out. The presence of Ag^+ may be confirmed in the usual way,

viz., by extracting the filter paper with NH_4OH and reprecipitating the AgCl by HNO_3 .

The retention of Ag^+ by the mercury residue is explained as follows: Finely divided mercury is more reactive than white mercury and tends to displace Ag from AgCl , as follows:



As thus represented, the replacement reaction itself is reversible, but the fact that the products on the right side of the equation are removed as fast as they are formed makes the reaction practically quantitative.

Exercises

1. Criticize the following definition: Group I consists of the cations whose chlorides are insoluble in water. What two cations of Group II might be included under such a definition?

2. Why is dilute HCl used in preference to water to wash Group I precipitates?

3. The iodides of Group I ions are less soluble than the chlorides. Consult the solubility table, and state why an iodide (*e.g.*, NH_4I) is not used as the group reagent.

4. Calculate the percentage composition of 6 *M* HCl (specific gravity, 1.12).

5. Which is the better confirmatory test for Pb^{++} , $\text{Cr}_2\text{O}_7^{--}$ or SO_4^{--} ? Why?

6. How many grams of PbCl_2 are carried into Group II in a 40-cc. filtrate, if the solubility of PbCl_2 is 0.04 mole per liter?

7. In an unknown containing Ag^+ and Ba^{++} , the Group I precipitate was not thoroughly washed. What error resulted?

8. Criticize the use of Na_2HPO_4 solution as a reagent in the confirmatory test for Pb^{++} .

9. Sometimes, in the extraction of AgCl by NH_4OH , in the analysis of Group I, a turbid filtrate is obtained. What is it? Does it interfere with the Ag^+ test? Explain.

10. An unknown solution gave with dilute HCl a white precipitate practically insoluble in excess acid. This precipitate was washed with a small amount of hot water, leaving a residue undissolved by NH_4OH . Interpret.

11. Arrange the following compounds in the order of their decreasing Pb^{++} concentration: $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{Pb}(\text{NO}_3)_2$, PbSO_4 , PbS , PbCl_2 , Na_2PbO_2 . Defend your conclusions by citing experimental evidence.

12. PbSO_4 is soluble in NaOH solution. Why is it not also soluble in NH_4OH ?

13. In Group I analyses, why are large excesses of HCl to be avoided?

14. Suppose an unknown contains Ag^+ in the presence of a large excess

of Hg_2^{++} . Explain why the usual test for Ag^+ should be negative. How should the test be made?

15. How many reactions can you cite in which the Hg_2^{++} ion breaks down into Hg^{++} and free Hg ?

16. Complete and balance the following equation for the oxidation of a $\text{Hg}_2(\text{NO}_3)_2$ solution by air: $\text{Hg}_2^{++} + \text{H}^+ + \text{O}_2 \rightarrow \text{Hg}^{++}$, etc.

17. The usual 4 cc. of 6 *M* HCl is used in precipitating Group I. To what volume should the mixture be diluted to make the PbCl_2 as insoluble as possible?

18. How would you separate HgCrO_4 from PbCrO_4 ?

19. Formulate equations for the equilibriums existing in a mixture made by adding dilute HCl (6 molar) to an excess of solid Hg_2Cl_2 .

20. What cations are indicated in the following Group I unknowns? (a) Dilute HCl was added to a hot solution of a Group I unknown without effect. A white precipitate formed upon cooling. (b) An unknown solution gave with dilute HCl a white precipitate insoluble in hot water but partially soluble in NH_4OH , leaving a black residue.

21. Identify the following ions of Group I: (a) an ion whose chloride is insoluble in hot water and in NH_4OH ; (b) an ion whose chromate is soluble in $\text{HC}_2\text{H}_3\text{O}_2$ and whose chloride is soluble in $\text{Na}_2\text{S}_2\text{O}_3$ solution; (c) an ion whose chloride is insoluble in hot water but soluble in aqua regia.

22. What volume of 6 *M* HCl would be required to precipitate the Ag^+ in 1.7 g. of AgNO_3 ?

23. Four cubic centimeters of 6 *M* HCl was added to 50 cc. of 0.5 *M* $\text{Hg}_2(\text{NO}_3)_2$, and the precipitated Hg_2Cl_2 was filtered off. What was the composition of the filtrate?

24. What weight of PbCrO_4 is formed when a solution of 2.94 g. of $\text{K}_2\text{Cr}_2\text{O}_7$ is added to a solution of 13 g. of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$?

25. What volume of 15 *M* NH_4OH would be required to dissolve the AgCl formed from 0.34 g. of AgNO_3 (mol. wt., 170)?

26. Five cubic centimeters of 0.2 *M* AgNO_3 is thoroughly shaken with 0.558 g. of PbCl_2 suspended in water. What will be the composition of the final precipitate and the final solution?

27. A 0.3 *M* $\text{Hg}_2(\text{NO}_3)_2$ solution contains 0.2 mole of free HNO_3 per liter. How many cubic centimeters of 6 *M* NH_4OH will be required to react completely with 4 cc. of this solution?

28. What volume of 6 *M* NH_4OH will be required to react completely with a mixture of 2 cc. of 0.3 *M* $\text{Hg}_2(\text{NO}_3)_2$, 3 cc. of 0.2 *M* AgNO_3 , and 2 cc. of 6 *M* HNO_3 ?

29. How many cubic centimeters of 6 *M* HCl will be required to precipitate Group I from a solution containing 2 cc. of 0.2 *M* AgNO_3 and 1 cc. of 0.3 *M* $\text{Hg}_2(\text{NO}_3)_2$?

CHAPTER XV

GROUP II—THE HYDROGEN SULFIDE GROUP

This group contains the cations, not in Group I, whose sulfides are precipitated by H_2S in the presence of dilute acids ($0.25 - 0.30 \text{ M H}^+$).

Mercuric, Hg^{++}	Arsenious, As^{+++}
Lead, Pb^{++}	Arsenic, As^{+++++}
Bismuth, Bi^{+++}	Antimonious, Sb^{+++}
Cupric, Cu^{++}	Antimonic, Sb^{+++++}
Cadmium, Cd^{++}	Stannous, Sn^{++}
	Stannic, Sn^{+++++}
	[Gold, Au^{+++}]
	[Platinum, Pt^{+++++}]

Rare and expensive elements, not included in ordinary analytical procedures, are designated by brackets.

These elements are divided into subgroups on the basis of the solubility of their sulfides in alkaline sulfide solutions (see page 227).

MERCURY (MERCURIC)

For the properties of the metal and the mercurous series, see pages 181 to 184.

Mercuric Compounds

Mercury is divalent throughout this series and resembles copper and cadmium, whereas mercurous mercury resembles silver and univalent gold.

The Ion.—The Hg^{++} ion is colorless, and all its compounds are exceedingly poisonous. It forms complex ions with the halogens, cyanide, and ammonia, making its reactions appear somewhat irregular.

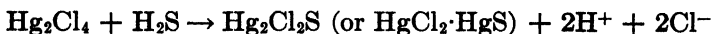
Soluble and Insoluble Compounds.—The important soluble Hg^{++} salts are the chloride, HgCl_2 , and the nitrate, $\text{Hg}(\text{NO}_3)_2$. They are obtained by dissolving metallic mercury in aqua regia

and in hot HNO_3 respectively (see Mercury, page 181). Other soluble salts are $\text{Hg}(\text{CN})_2$, $\text{Hg}(\text{ClO}_4)_2$, and $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$. Of the insoluble compounds, HgS is the most important. Met less frequently in analytical procedures are HgNH_2Cl , HgCrO_4 , etc.

Mercuric Chloride.— HgCl_2 is a white salt, soluble in water and also soluble in alcohol. This solubility in alcohol is surprising, for nondeliquescent compounds are usually insoluble in alcohol. Solutions of HgCl_2 are rather poor conductors of the electric current, indicating slight ionization—much less than that of $\text{Hg}(\text{NO}_3)_2$. This low ionization manifests itself in several ways. For example, HgCl_2 gives no reaction with $\text{K}_2\text{Cr}_2\text{O}_7$ solution, but $\text{Hg}(\text{NO}_3)_2$ forms yellow HgCrO_4 ; FeSO_4 reduces $\text{Hg}(\text{NO}_3)_2$ to metallic mercury but has no effect on HgCl_2 .

Mercuric Nitrate.—This salt is formed when mercury is dissolved in hot, concentrated HNO_3 (see page 181). Owing to its tendency to hydrolyze, forming basic salts, free HNO_3 is added in making up its solutions.

Mercuric Sulfide.— Hg^{++} ions react with an excess of S^{--} ions, forming black HgS . If an HgCl_2 solution is treated with H_2S in small amounts (*e.g.*, by adding H_2S solution slowly to the Hg^{++} solution, with constant stirring), the precipitate obtained is first white, then yellow, brown, and finally black. These intermediate forms have been considered mixed salts, as, for example, $\text{HgCl}_2 \cdot 2\text{HgS}$. There is reason to suspect that mercuric chloride exists in solution in polymerized forms, such as Hg_2Cl_4 , etc. This would make possible a number of reactions, giving a variety of precipitates; *e.g.*,



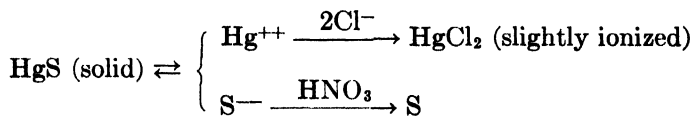
These mixed salts react with excess H_2S , giving eventually black HgS .

Mercuric sulfide is insoluble in HCl and in dilute HNO_3 . The insolubility of HgS in boiling 2 *M* HNO_3 is used to separate HgS from the other sulfides of the copper subgroup. If the acid is allowed to become concentrated by prolonged boiling, the HgS may begin to react, forming first a white mixed salt, $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{HgS}$.

Mercuric sulfide is readily dissolved by aqua regia, thus:



Some have tried to explain this reaction by assuming that the nascent chlorine given off by the aqua regia is a *stronger* oxidizing agent than HNO_3 . It does not stand to reason that a reducing agent (for HCl does act as a reducing agent toward strong oxidizing agents) can be mixed with an oxidizing agent, giving a product of greater oxidizing potential. Such an assumption is certainly contrary to the law of mixtures. More probably the solution of HgS by aqua regia is a matter of teamwork. HgS is exceedingly insoluble, and the concentrations of Hg^{++} and S^{--} present in a saturated solution of HgS are too small for either HNO_3 or Cl^- , acting alone, to have any effect; but acting together, they are able to bring about the solution of HgS .



It should be noticed that the low ionization of HgCl_2 is the decisive factor. HgS will not dissolve if for the HCl is substituted an acid (*e.g.*, HClO_4) that forms a well-ionized salt, such as $\text{Hg}(\text{ClO}_4)_2$.

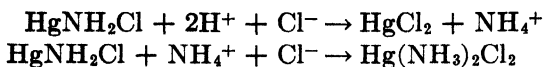
Mercuric sulfide is almost insoluble in $(\text{NH}_4)_2\text{S}$ but is readily soluble in concentrated Na_2S or K_2S . Probably some kind of mercuri-sulfide complex ion is formed; *e.g.*, $\text{HgS} + \text{S}^{--} \rightleftharpoons \text{HgS}_2^{--}$. The difference may be due to the fact that $(\text{NH}_4)_2\text{S}$ gives a much lower concentration of S^{--} than Na_2S and K_2S . Upon acidification (partially upon dilution) the HgS is reprecipitated, owing to the removal of the S^{--} from the left-hand side of the equation.

Reactions with Ammonia.— NH_3 solutions react with soluble mercuric compounds, forming a variety of products. Some of these contain the amino group NH_2 ; others contain the ammonia group NH_3 .

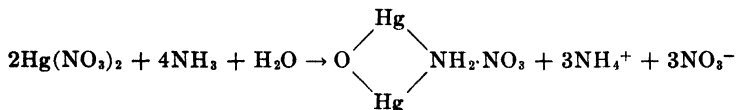
From HgCl_2 solution, NH_3 precipitates white mercuric amino chloride, HgNH_2Cl .



This compound is soluble in acids and in NH_4Cl solution. For example,

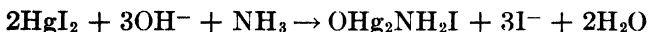


With $\text{Hg}(\text{NO}_3)_2$ solution, NH_3 forms white oxyamino mercuric nitrate.



The radical $\text{OHg}_2\text{NH}_2^+$ occurs in a number of compounds. Its hydroxide is sometimes called "Millon's base."

With HgI_2 (dissolved in KI-KOH solution), NH_3 precipitates the iodide of Millon's base.

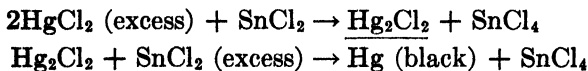


This is a very insoluble brown precipitate, and its formation is used as a very sensitive test for the NH_4^+ ion (see page 306).

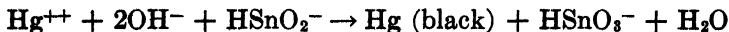
Stable Halide Compounds.—Mercuric chloride and mercuric bromide are soluble, but their solutions conduct the electric current very slightly. A molar solution of HgCl_2 is ionized less than 1 per cent. Consequently, Cl^- and Br^- remove Hg^{++} from solution almost completely (see solubility of HgS in aqua regia, page 189). Hg^{++} and I^- ions combine, forming scarlet mercuric iodide, HgI_2 , insoluble in water, but easily soluble in excess I^- ions: $\text{HgI}_2 + 2\text{I}^- \rightarrow \text{HgI}_4^{--}$ (colorless).

Mercuric cyanide, $\text{Hg}(\text{CN})_2$, is another soluble mercuric salt that is very stable because of low ionization. As a result, many mercuric compounds insoluble in water dissolve readily in CN^- solutions; *e.g.*, $\text{HgO} + 2\text{CN}^- + \text{H}_2\text{O} \rightarrow \text{Hg}(\text{CN})_2 + 2\text{OH}^-$.

Reduction.—Mercuric compounds are weak oxidizing agents and may be reduced by active reducing agents to the Hg_2^{++} stage or even to metallic mercury. SnCl_2 is most frequently used for this purpose.



The reduction takes place more readily in alkaline medium; *e.g.*,



Compare the Bi^{+++} ion (page 198).

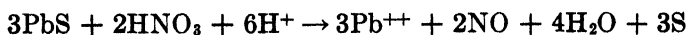
Detection.—The Hg^{++} ion is almost always detected by its formation of white-to-gray precipitate with SnCl_2 solution. Since SnCl_2 may give precipitates with many other solutions (*e.g.*, Ag^+ , Cu^{++} , etc.), the Hg^{++} ion must previously be separated by the insolubility of its sulfide in 2 *M* HNO_3 . The formation of red HgI_2 is not dependable, owing to its solubility in excess I^- ions. Sometimes Hg^{++} is tested for by placing a drop of the solution on a bright piece of copper foil. The Hg^{++} ion is displaced as a gray deposit, which takes on a silver luster upon gentle polishing.

LEAD

The properties of the metal and the reactions involved in the analysis of Group I have been given on pages 174 to 178. Several new reactions appearing in Group II will be considered here.

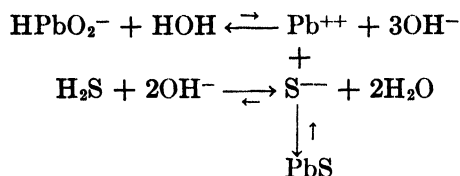
Incomplete Separation in Group I.—As stated on page 176, PbCl_2 has a solubility of 0.04 mole per liter in water at room temperature. Its solubility is greater in the presence of tartrates, acetates, etc., which form soluble complexes with the Pb^{++} ion. As a result, Pb^{++} ions are never completely precipitated in Group I but are always refound in Group II. Sometimes—particularly when present in small amount—they are found in Group II only. Even if found in Group I, their presence in Group II must be taken into account since they interfere with the tests for other ions, *viz.*, Bi^{+++} , Cu^{++} , and Cd^{++} .

Lead Sulfide.— Pb^{++} ions combine with S^{--} ions, forming black PbS , insoluble in dilute acids and in $(\text{NH}_4)_2\text{S}$. Its solubility in water is the smallest of all the common Pb^{++} salts—only 2×10^{-14} mole per liter. Still it is considerably soluble in concentrated HCl , owing to two influences: (1) the low ionization of the H_2S formed, and (2) complexing of the Pb^{++} ions by the excess Cl^- , possibly as PbCl_4^{--} . Another solvent for PbS is warm dilute HNO_3 .



PbS is also precipitated by H_2S from alkaline solutions containing the plumbite ion, HPbO_2^- . This anion gives a certain Pb^{++} concentration in the solution, though much less than that maintained by PbCl_2 . However the alkalinity increases the concen-

tration of the S^- ion to an extent that about compensates for the loss in Pb^{++} ions.



Lead Sulfate.— $PbSO_4$ is formed as a white microcrystalline precipitate when solutions of Pb^{++} and SO_4^{--} ions are mixed.

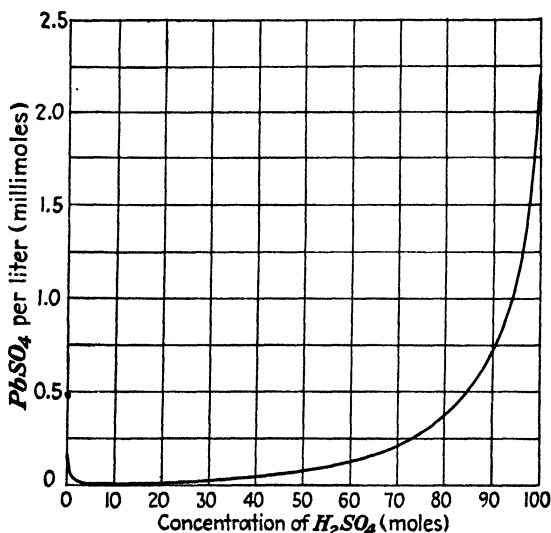
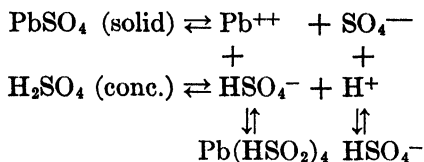


FIG. 25.—Solubility of lead sulfate in sulfuric acid.

Its solubility in water at 25° is 0.0015 mole per liter. This solubility is not so small as might be desired for a "clean" separation by precipitation; however, the solubility may be reduced considerably by an excess of SO_4^{--} ions—another application of the common-ion effect.

Lead sulfate is surprisingly soluble in concentrated H_2SO_4 . This seems to be due to the ionization of the concentrated acid being limited almost wholly to the primary stage; *i.e.*, H_2SO_4 (conc.) $\rightleftharpoons H^+ + HSO_4^-$. The concentration of the SO_4^{--} ions is very small—much less than that furnished by the ionization of

PbSO_4 . Consequently the equilibrium in the ionization of the salt is displaced by the withdrawal of SO_4^{--} ions, so that its solubility is considerably increased.



Upon dilution with water, the concentration of SO_4^{--} is vastly

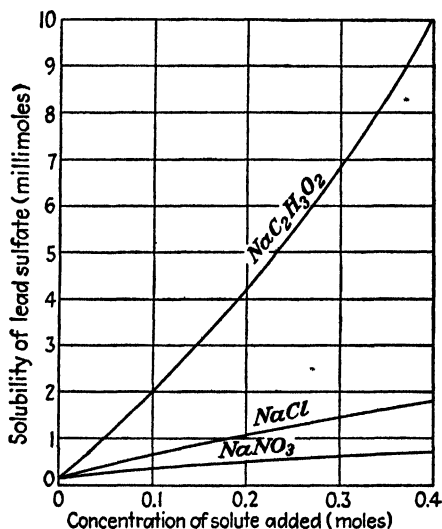
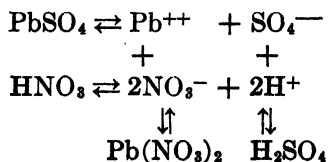


Fig. 26.—Solubility of lead sulfate in electrolytes.

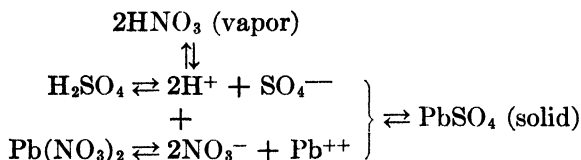
increased at the expense of the HSO_4^- ions, with the result that the SO_4^{--} recombines with the Pb^{++} , reprecipitating PbSO_4 .

The solubility of PbSO_4 is increased by the presence of many electrolytes, in some cases very considerably (Fig. 26). This increase was formerly explained as due to the formation of molecules of Pb^{++} salts and of sulfates. For example,



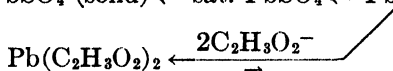
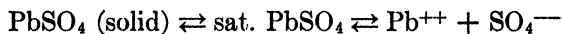
The increase in solubility, according to this theory, is in the form of molecules of $\text{Pb}(\text{NO}_3)_2$ and H_2SO_4 , leaving the number of Pb^{++} and SO_4^{--} ions in the solution approximately constant. The complete ionist, of course, cannot accept such an explanation. His theory is that the solvent power of water is increased by the presence of electrolytes (the "salt effect"). This increase in solubility by added electrolytes may conveniently be called the *uncommon-ion effect*. Numerous cases of the phenomenon will be met in analytical procedures.

Conversion of $\text{Pb}(\text{NO}_3)_2$ into PbSO_4 .—As has already been shown, Pb^{++} ions cannot be completely precipitated as PbSO_4 in the presence of HNO_3 . The latter may be removed by adding H_2SO_4 and evaporating. The equilibriums involved may be represented:



As the temperature rises, the molecules with the highest vapor pressure (*i.e.*, HNO_3) will first reach their boiling point and distill out of the mixture. Molecular H_2SO_4 and $\text{Pb}(\text{NO}_3)_2$ will constantly adjust their ionizations to maintain a supply of H^+ and NO_3^- ions, until the supply of one of them [the $\text{Pb}(\text{NO}_3)_2$] is exhausted. This procedure for the displacement of a low-boiling acid by a high-boiling acid is perfectly general. It should be noted that the displacing acid is not necessarily stronger than the acid displaced. H_3PO_4 will also displace HNO_3 . It is a matter of boiling points, not ionization.

Lead Acetate.— PbCl_2 , PbSO_4 , etc., are soluble in $\text{C}_2\text{H}_3\text{O}_2^-$ solutions. $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ is a much better solvent than $\text{HC}_2\text{H}_3\text{O}_2$; for the former gives a high concentration of $\text{C}_2\text{H}_3\text{O}_2^-$ ions, and the latter gives a very low one. This solubility is generally explained as due to the formation of slightly ionized molecules of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. It is possible that the product may be the complex ion $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_3^-$ and not the molecule. The solvent action of $\text{C}_2\text{H}_3\text{O}_2^-$ ions on PbSO_4 precipitates may be diagrammed as follows:



The relative lengths of the arrows are intended to show that the concentration of Pb^{++} from the $\text{Pb(C}_2\text{H}_3\text{O}_2)_2$ ion is less than that from the PbSO_4 molecule, although $\text{Pb(C}_2\text{H}_3\text{O}_2)_2$ is a fairly soluble substance. The concentration of Pb^{++} ions in the presence of $\text{C}_2\text{H}_3\text{O}_2^{--}$ ions is not small enough to prevent the precipitation of PbS when H_2S is added or of PbCrO_4 when CrO_4^{--} is added.

Lead Tartrate.—Several other ions behave like $\text{C}_2\text{H}_3\text{O}_2^{--}$, forming with Pb^{++} ions soluble products of low ionization. Of these the tartrate ion $\text{C}_4\text{H}_4\text{O}_6^{--}$ is the most important.

Lead Chromate.—One of the most distinctive reactions of the Pb^{++} ion is the precipitation of yellow PbCrO_4 , insoluble in $\text{HC}_2\text{H}_3\text{O}_2$, but soluble in HCl and HNO_3 . This salt is used as a pigment under the trade name "chrome yellow." Its solubility in water is low— 1.3×10^{-7} mole per liter. The reagent commonly used in its precipitation is potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$. The question immediately arises, Why PbCrO_4 instead of PbCr_2O_7 ? Dichromate solutions have been extensively studied, and the best results indicate that the solutions contain equilibrium mixtures of $\text{Cr}_2\text{O}_7^{--}$, HCrO_4^- , and CrO_4^{--} ions. The equilibria involved may be represented thus:

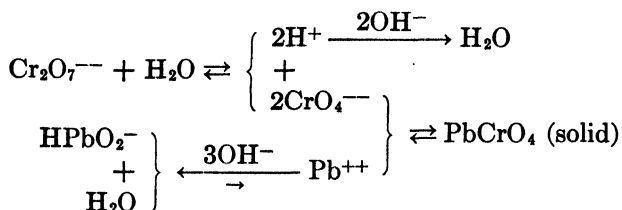


Of these three anions, CrO_4^{--} seems to be the only one present in sufficient concentration to give a precipitate with ordinary concentrations of Pb^{++} . Lead hydrogen chromate, $\text{Pb(HCrO}_4)_2$, if it exists at all, seems to be soluble. PbCr_2O_7 may be precipitated under the proper conditions, *e.g.*, when a Pb^{++} solution is treated with a concentrated solution of chromic acid, $\text{H}_2\text{Cr}_2\text{O}_7$.

This is another case of displacement of equilibrium in accordance with the Le Châtelier principle. There are two stresses to be considered here: (1) the effect of excess water, which shifts both of the above equilibria rightward; and (2) the effect of H^+ ions, which shifts the second equilibrium leftward, with the result that the chromate is present mainly as HCrO_4^- . $\text{H}_2\text{Cr}_2\text{O}_7$ seems to be a rather weak acid, or else the $\text{Cr}_2\text{O}_7^{--}$ ions hydrate

very rapidly. At any rate, the concentration of these anions is usually very low.

Lead chromate is easily soluble in NaOH solution. The effect of OH^- ions on the above equilibrium is the removal of the H^+ ions and the consequent increase of the concentration of the CrO_4^{--} ions. This action favors the precipitation of PbCrO_4 . It is more than offset, however, by tying the Pb^{++} ions up as plumbite ions, HPbO_2^- .



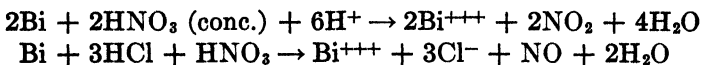
This is a very satisfactory reaction for separating PbCrO_4 and $(\text{BiO})_2\text{Cr}_2\text{O}_7$.

Detection.— Pb^{++} ions are usually separated by precipitation as PbSO_4 , soluble in $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$. From this solution, Pb^{++} is precipitated by CrO_4^{--} as PbCrO_4 , soluble in NaOH solution.

BISMUTH

Bismuth differs from its companion elements of Group V of the Periodic Table, arsenic and antimony, in being almost wholly metallic in its behavior and showing little tendency to enter into anions.¹

The Metal.—Bismuth is a brittle, crystalline metal, with a reddish sheen. It dissolves in oxidizing solvents, such as HNO_3 and aqua regia.



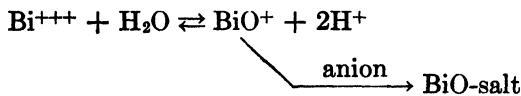
The Ions.—Bismuth forms two ions: the trivalent bismuth ion Bi^{+++} and the univalent bismuthyl ion BiO^+ .

Soluble and Insoluble Compounds.—The most important of the soluble compounds are the salts BiCl_3 , $\text{Bi}(\text{NO}_3)_3$, and

¹ An exception is the bismuthates (*e.g.*, sodium bismuthate, NaBiO_3), in which the element is pentavalent. These compounds are unstable and are vigorous oxidizing agents.

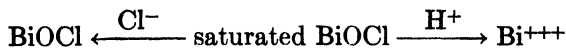
$\text{Bi}_2(\text{SO}_4)_3$. Since these are considerably hydrolyzed by water, forming insoluble bismuthyl salts, dilute acids are used as the actual solvents. In addition to these, the most important insoluble compounds are the hydroxide, $\text{Bi}(\text{OH})_3$, and the sulfide, Bi_2S_3 .

Bismuthyl Compounds.—When an acid solution of a Bi^{+++} salt is diluted with water, a white precipitate is formed. Such precipitates are considered to be salts of the bismuthyl ion BiO^+ formed by the decomposition of water.



The equilibrium may be shifted to the right by adding water and to the left by adding H^+ ions—i.e., acids. Bismuthyl salts are also called *basic* and *oxy* salts. For example, BiONO_3 is called “bismuthyl nitrate,” “basic bismuth nitrate” and “bismuth oxynitrate.”

It is to be noted that whereas the addition of acids tends to dissolve a bismuthyl salt, the addition of a common ion represses its solubility. Illustrating by bismuthyl chloride,



The mass law serves to indicate the resultant of these two opposing actions. Considering the total equation $\text{Bi}^{+++} + \text{Cl}^- + \text{H}_2\text{O} \rightleftharpoons \text{BiOCl} + 2\text{H}^+$, the mass law expression takes the form

$$\frac{[\text{BiOCl}][\text{H}^+]^2}{[\text{Bi}^{+++}][\text{Cl}^-][\text{H}_2\text{O}]} = K_{\text{equilibrium}}$$

Since BiOCl is sparingly soluble, $[\text{BiOCl}]$ represents the concentration of a saturated solution and therefore may be regarded as a constant. Water is present in such large amount that its concentration undergoes no appreciable change, so that it may also be considered constant. The expression may therefore be put in the simpler form

$$\frac{[\text{H}^+]^2}{[\text{Bi}^{+++}][\text{Cl}^-]} = K_{\text{equilibrium}}$$

Solving for $[\text{Bi}^{+++}]$, which may be taken as a measure of the amount of the salt dissolved,

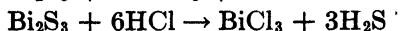
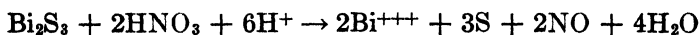
$$[\text{Bi}^{+++}] = k \frac{[\text{H}^+]^2}{[\text{Cl}^-]}$$

That is, in dissolving BiOCl in dilute HCl , H^+ ions favor the reaction and Cl^- ions oppose it. But the effect of the H^+ ions is greater, since it varies as the *square* of the concentration, while the effect of the Cl^- ion varies as the *first power*.

NaOH solution is very effective in reducing the solubility of BiCl_3 , for the OH^- ion both reduces the H^+ -ion concentration and furnishes OH^- ions for the formation of the insoluble BiOOH [or $\text{Bi}(\text{OH})_3$].

Bismuth Hydroxide.— Bi^{+++} ions are precipitated by dilute bases, forming white $\text{Bi}(\text{OH})_3$ (or BiOOH). This precipitate is soluble in strong acids and very slightly soluble in hot concentrated alkalis: $\text{Bi}(\text{OH})_3 + \text{OH}^- \rightleftharpoons \text{BiO}_2^-$ (bismuthite anion) $+ 2\text{H}_2\text{O}$. $\text{Bi}(\text{OH})_3$ is insoluble in NH_4OH , forming no complex ion with NH_3 . For these reasons, it is usually precipitated by NH_4OH . Like $\text{Sb}(\text{OH})_3$, it is soluble in certain organic substances, such as tartrates and glycerol.

Bismuth Sulfide.— Bi^{+++} ions are precipitated by H_2S as brown Bi_2S_3 , insoluble in dilute acids and in $(\text{NH}_4)_2\text{S}$ or Na_2S . It is soluble in hot dilute HNO_3 and in hot concentrated HCl .



Bismuth Phosphate.—Soluble phosphates precipitate Bi^{+++} ions as white BiPO_4 , insoluble in dilute HNO_3 .

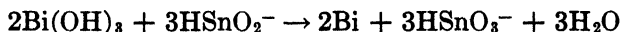
Bismuthyl Dichromate.—Excess of $\text{K}_2\text{Cr}_2\text{O}_7$ precipitates Bi^{+++} as yellow bismuthyl dichromate, $(\text{BiO})_2\text{Cr}_2\text{O}_7$.



It may be distinguished from PbCrO_4 by its insolubility in NaOH solution.

Reduction of Bismuth Compounds.—The position of bismuth in the e.m.f. series suggests that its compounds should be easily reduced. Sodium stannite¹ solution reduces bismuth hydroxide to black metallic bismuth.

¹ See page 223 for precautions in preparing this solution.



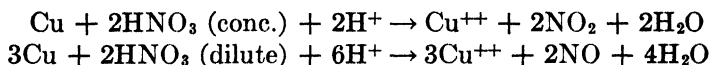
On the contrary, Bi^{+++} ions are not reduced by SnCl_2 . The solution must be alkaline for reduction to take place.

Detection.—The most important reaction used in the detection of Bi^{+++} ions is the formation of black bismuth by HSnO_2^- , described in the preceding paragraph. This test is not specific and should not be made on the original substance, for Hg^{++} , Hg_2^{++} , and Ag^+ ions also give black precipitates with HSnO_2^- ions.

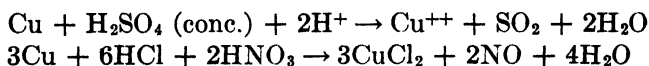
COPPER

The Metal.—Copper is a red metal, extensively used in electrical apparatus. It is a constituent of many alloys, such as the brasses and bronzes.

The proper solvent for metallic copper is HNO_3 . When concentrated HNO_3 is used, brown NO_2 is evolved; when dilute HNO_3 is used, colorless NO is the product.



It is also soluble in concentrated H_2SO_4 and in aqua regia.



The last reaction is favored, very probably, by the withdrawal of the CuCl_2 by excess Cl^- , with the formation of a complex ion, as CuCl_3^- or CuCl_4^{--} . Copper is insoluble in nonoxidizing acids— HCl , dilute H_2SO_4 , dilute HClO_4 , etc. This behavior is in line with the position of copper in the e.m.f. series.

Series of Compounds.—Copper forms two series of compounds: (1) the *cuprous*, in which the average valence is $+1$; and (2) the *cupric*, in which the valence is $+2$.

Cuprous Compounds

The Cuprous Ion.—The formula of the cuprous ion is sometimes written Cu^+ , assuming a simple monovalence. Most authorities prefer to consider it a double ion with the formula Cu_2^{++} (cf. the mercurous ion Hg_2^{++}). Cuprous compounds are, with a few important exceptions, white in color. This would

indicate that the cuprous ion is colorless. This may not be conclusive, for the ion forms no soluble compounds that ionize simply, giving Cu_2^{++} ions.

Solubilities.—Cuprous salts are generally insoluble in water but are soluble in concentrated halogen acids, forming colorless solutions. Most cuprous precipitates are soluble in NH_3 solutions, forming a colorless complex ion—possibly $\text{Cu}(\text{NH}_3)_2^+$ or $\text{Cu}_2(\text{NH}_3)_4^{++}$. From the analytical point of view, the most important of the insoluble compounds are the iodide, the thiocyanate, the oxide, and the sulfide.

Cuprous Chloride.—An HCl solution of this salt is prepared by heating a solution of cupric chloride and HCl with metallic copper until the solution is colorless.

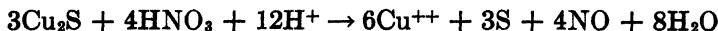


Upon dilution of the mixture with water that has been freshly boiled to expel the air, white Cu_2Cl_2 is precipitated. The solubility of Cu_2Cl_2 in concentrated HCl is evidently due to the formation of a cuprochloride complex ion; possibly, $\text{Cu}_2\text{Cl}_2 + 2\text{Cl}^- \rightarrow 2\text{CuCl}_2^-$.

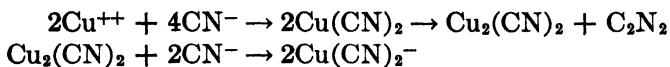
Cuprous Iodide.—This is a white salt, formed by the spontaneous decomposition of cupric iodide, as follows: $2\text{CuI}_2 \rightarrow \text{Cu}_2\text{I}_2 + \text{I}_2$. It is one of the few cuprous compounds that is stable in contact with the air. It is soluble in an excess of I^- ions, forming cupriiodide ions CuI_2^- .

Cuprous Thiocyanate.—This is another cuprous compound that is stable in the air. It is formed as a white precipitate when Cu^{++} ions are reduced in the presence of SCN^- ions. Its formula is written $\text{Cu}_2(\text{SCN})_2$.

Cuprous Sulfide.— Cu_2^{++} -compounds are precipitated by H_2S as black Cu_2S , soluble in warm HNO_3 .

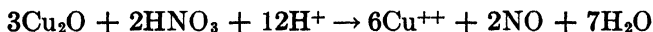


Cuprous Cyanide.—This is a white salt, with the formula $\text{Cu}_2(\text{CN})_2$. It may be formed by adding an alkaline cyanide to an ammoniacal solution of a cupric salt. Cupric cyanide is first formed, which decomposes into cuprous cyanide, $\text{Cu}_2(\text{CN})_2$, and cyanogen, C_2N_2 . The $\text{Cu}_2(\text{CN})_2$ dissolves in excess CN^- ions, forming the colorless cuprocyanide anion $\text{Cu}(\text{CN})_2^-$. Equations are as follows:



The cuprocyanide ion is very stable, *i.e.*, it dissociates very slightly into Cu_2^{++} and CN^- . This dissociation is so slight that $\text{Cu}(\text{NH}_3)_4^{++}$ is easily converted into $\text{Cu}(\text{CN})_2^-$ and C_2N_2 by CN^- ions. Again, the dissociation of $\text{Cu}(\text{CN})_2^-$ is so slight that it does not give a high enough concentration of Cu_2^{++} to form Cu_2S with H_2S .

Cuprous Oxide.—Cuprous hydroxide seems to be unstable, breaking down into red cuprous oxide, Cu_2O , and H_2O . The oxide is soluble in dilute HNO_3 , forming a cupric solution.



Cuproammonia Complex Ion.—Cuprous salts are soluble in NH_3 solutions, forming what may be considered the colorless complex cuproammonia ion $\text{Cu}(\text{NH}_3)_2^+$. Solutions containing this ion take up oxygen from the air, forming the blue cupriammonia ion $\text{Cu}(\text{NH}_3)_4^{++}$.

Reducing Action.—Cuprous compounds are vigorous reducing agents. For example, they will reduce Hg^{++} to Hg_2^{++} and Hg , Fe^{+++} to Fe^{++} , and H_3AsO_4 to H_3AsO_3 . Air oxidizes them to Cu^{++} ions. For this reason, they are never met in the course of a cation analysis, except in the formation of the cuprocyanide ion in separating Cd^{++} as CdS . Even if they were present in the original material, they would be oxidized to Cu^{++} by the air or by HNO_3 before Group II is reached. Their presence in the original material must be inferred from its properties.

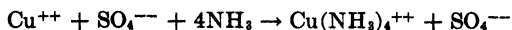
Cupric Compounds

The Ion.—The blue color of cupric solutions is due to a hydrated ion, sometimes written $\text{Cu}(\text{H}_2\text{O})_4^{++}$. The anhydrous forms of the salts are brown (as CuBr_2) or white (as CuSO_4).

Soluble and Insoluble Compounds.—The most common of the soluble cupric salts are CuCl_2 , $\text{Cu}(\text{NO}_3)_2$, CuSO_4 , and $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$. The insoluble cupric compounds usually met in analytical work are CuS , $\text{Cu}(\text{OH})_2$, CuO , and $\text{Cu}_2\text{Fe}(\text{CN})_6$.

Cupric Sulfide.— H_2S precipitates from mildly acid solution black CuS . The precipitate is insoluble in dilute HCl and in dilute H_2SO_4 . It dissolves readily in hot dilute (2 *M*) HNO_3 .

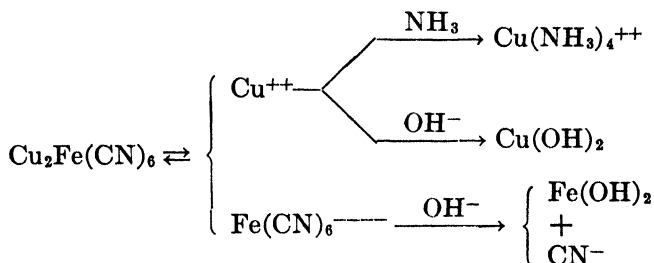
Or better, written ionically,



$\text{Cu}(\text{NH}_3)_4^{++}$ ions are very stable; yet they do dissociate to a sufficient extent to give enough Cu^{++} ions to react with H_2S and a few other reagents.

Cupric Cyanide.—Alkaline cyanides combine with Cu^{++} ions, forming first yellow cupric cyanide, $\text{Cu}(\text{CN})_2$, which decomposes into cuprous cyanide, $\text{Cu}_2(\text{CN})_2$, and cyanogen, $(\text{CN})_2$. The $\text{Cu}_2(\text{CN})_2$ then dissolves in excess CN^- ions, forming the cuprocyanide anion $\text{Cu}(\text{CN})_2^-$.

Cupric Ferrocyanide.—One of the most insoluble of the cupric compounds is $\text{Cu}_2\text{Fe}(\text{CN})_6$. This is formed as a mahogany-red precipitate when $\text{Fe}(\text{CN})_6^{--}$ ions are added to a neutral or acid solution of Cu^{++} . It is decomposed by NH_4OH or strong bases, owing to a combination of destructive actions.



It is doubtful if any one of these alone would be sufficient to decompose the compound.

If only a trace of Cu^{++} is present, the $\text{Cu}_2\text{Fe}(\text{CN})_6$ will appear, not as a precipitate, but as a rose-colored solution. This is not a true solution but a sol (see page 24). It will be remembered that sol formation is characteristic of compounds of very high insolubility.

Displacement.—The e.m.f. table indicates that Cu^{++} ions should be displaced from solution by any metal above it in the list. Iron is usually employed, for the following reasons: (1) Since the purpose of the displacement is the separation from Cd^{++} , the displacing metal must be below cadmium. (2) It should be as high as possible in the list so as to make the action as vigorous as possible. (3) But, most important of all, the sulfide of the

metal must be as soluble as possible, so that it will not precipitate easily in dilute acid solution. Iron is much better in all these respects than nickel, cobalt, tin, or lead.

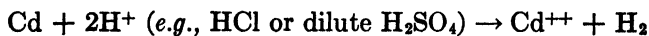
Detection.—The presence of Cu^{++} ions is indicated by the following reactions: (1) A blue color in the solution of the Copper subgroup is a sufficient test for Cu^{++} ions. The other ions of the subgroup are colorless. (2) A deep blue color with NH_4OH is a sensitive test for Cu^{++} , though it cannot be made on the original substance, owing to interference by Ni^{++} ions. (3) In case the NH_4OH test is negative, only a trace of Cu^{++} can be present. This may be detected by acidifying the solution with H_2SO_4 and adding a drop of $\text{K}_4\text{Fe}(\text{CN})_6$ solution. A rose-colored sol will indicate Cu^{++} if it is present as much as 1 in 250,000.

CADMIUM

This element belongs to the magnesium-zinc-cadmium-mercury group of the Periodic Table. Strangely, the ions of these elements are not found in the same group. This follows from wide differences in the solubilities of their sulfides. HgS is one of the most insoluble of all the sulfides, but MgS is so soluble that it is completely hydrolyzed by water.

The Metal.—Cadmium is a white metal, resembling zinc in most of its properties. It was formerly considered rare but recently has become available in fair quantities as a by-product in the refining of zinc. It is used commercially in certain low-melting alloys, in bearing metals and dental amalgams, and as a plate to protect other metals against corrosion.

As indicated by the e.m.f. table (page 150), cadmium is soluble in mineral acids.



It is also soluble in HNO_3 , but without the evolution of hydrogen.



Ions.—Cadmium is bivalent in all its compounds. The Cd^{++} ion is colorless and tends to form complex ions, such as $\text{Cd}(\text{NH}_3)_4^{++}$ and $\text{Cd}(\text{CN})_4^{--}$. There is reason for the belief that its halides are complexed to a greater or less extent; e.g., concentrated CdI_2 seems to contain CdI_4^{--} anions (*cf.* HgI_4^{--}), for the

element moves mainly to the anode during electrolysis of the iodide solution.

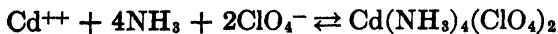
Soluble and Insoluble Compounds.—The Cd^{++} ion forms soluble salts with most of the commoner anions, such as Cl^- , Br^- , NO_3^- , ClO_4^- , SO_4^{--} , and $\text{C}_2\text{H}_3\text{O}_2^-$. The hydroxide, carbonate, sulfide, phosphate, etc., are insoluble in water but soluble in strong acids.

Cadmium Sulfide.—The most important analytical compound of Cd^{++} is the sulfide, CdS —yellow, soluble in concentrated strong acids, but insoluble in concentrations of $0.3\text{ }M\text{ H}^+$ or less. Its solubility at 25° is 6×10^{-15} mole per liter. It follows that the solubility product is 3.6×10^{-29} . The color of the precipitate varies with the method of formation. From neutral Cd^{++} solutions, H_2S precipitates light yellow CdS , difficult to filter. If the solution contains a free acid, such as HCl or H_2SO_4 , the precipitate is orange in color and filters well. Analysis of the orange precipitate shows that it is a mixed salt, perhaps $\text{CdCl}_2 \cdot \text{CdS}$ or $\text{CdSO}_4 \cdot \text{CdS}$. This indicates stepwise dissociation; *e.g.*, $\text{CdCl}_2 \rightleftharpoons \text{CdCl}^+ + \text{Cl}^-$, and $2\text{CdCl}^+ + \text{H}_2\text{S} \rightarrow (\text{CdCl})_2\text{S}$.

Cadmium Hydroxide.—When NaOH or KOH is added to a solution containing Cd^{++} ions, white $\text{Cd}(\text{OH})_2$ is precipitated, insoluble in excess of these bases [*cf.* $\text{Zn}(\text{OH})_2$, page 249].

Cadmium-ammonia Complex Ion.— Cd^{++} ions combine with NH_3 , forming the complex ion $\text{Cd}(\text{NH}_3)_4^{++}$. This complex ion is rather unstable, redissociating considerably into Cd^{++} and NH_3 . The concentration of Cd^{++} is sufficient for CdS to be completely precipitated by H_2S . Another corollary of the low stability of this complex is that only rather soluble cadmium compounds will dissolve in NH_3 solution—*e.g.*, $\text{Cd}(\text{OH})_2$ and CdCO_3 .

Cadmium-ammonia Perchlorate.—Solutions containing $\text{Cd}(\text{NH}_3)_4^{++}$ ions give with saturated NH_4ClO_4 solution a white crystalline precipitate of $\text{Cd}(\text{NH}_3)_4(\text{ClO}_4)_2$. This compound is only sparingly soluble in water, and its solubility may be further repressed by an excess of NH_3 molecules and ClO_4^- ions.

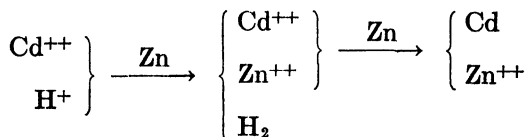


Hence it is desirable to have the NH_3 and NH_4ClO_4 present in excess. A limitation is the possibility of precipitating NH_4ClO_4 ,

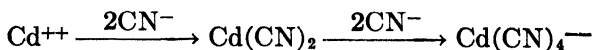
which has only a moderate solubility. This complication is avoided by using as a precipitant a concentrated solution of NH_4OH that has been saturated with NH_4ClO_4 .

Cadmium Ferrocyanide.—Alkaline ferrocyanides precipitate Cd^{++} as white $\text{Cd}_2\text{Fe}(\text{CN})_6$. This salt is not so insoluble as $\text{Cu}_2\text{Fe}(\text{CN})_6$; and consequently, when a drop of $\text{K}_4\text{Fe}(\text{CN})_6$ solution is added to a mixture of Cu^{++} and Cd^{++} ions, only the $\text{Cu}_2\text{Fe}(\text{CN})_6$ forms.

Displacement by Metals.—The Cd^{++} ion cannot be displaced from acidified solutions by more active metals; for it lies above hydrogen in the e.m.f. series, and therefore only the latter is affected. After the solution becomes neutral, the Cd^{++} may be displaced by active metals like zinc or aluminum. The successive steps may be thus expressed:



Cadmium Cyanide.—If a Cd^{++} solution is treated with increasing amounts of NaCN , a white precipitate of $\text{Cd}(\text{CN})_2$ is formed but later dissolves in excess of CN^- .



This complex ion is only moderately stable, giving enough Cd^{++} ions to react with H_2S and form yellow CdS .

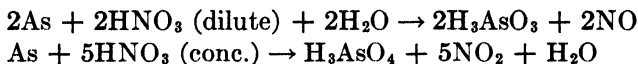
Detection.—Cadmium compounds show few conspicuous reactions that may be used for the detection of the element. The most important are: (1) The formation of yellow CdS . All the ions of the Copper subgroup interfere and must therefore be previously removed by precipitation or complex formation before this test is applied. (2) The precipitation of white $\text{Cd}(\text{NH}_3)_4(\text{ClO}_4)_2$. This is hard to see in the presence of deep-blue $\text{Cu}(\text{NH}_3)_4^{++}$ ions. This interference may be obviated by adding NaCN until the mixture is decolorized or by allowing the mixture to stand until the precipitate settles out.

ARSENIC

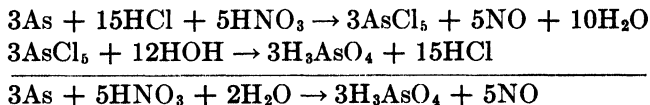
The Metal.—Arsenic is a brittle gray substance, with little physical resemblance to the metals. It evaporates at low tem-

peratures (about 615°) without melting. Consequently it cannot be made to enter into alloys in more than small amounts. Lead shot contains up to 0.5 per cent.

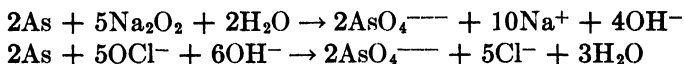
Arsenic is insoluble in HCl but dissolves readily in HNO₃. The products of the HNO₃ reaction depend upon concentration and temperature. In general, dilute HNO₃ converts it mainly into arsenious acid, H₃AsO₃, and concentrated HNO₃ gives arsenic acid, H₃AsO₄.



Aqua regia dissolves it readily. The reaction probably proceeds in steps, the second step regenerating the HCl formed in the first one.



Arsenic is also soluble in alkaline oxidizing agents, forming arsenates; *e.g.*,



Ions.—Arsenic forms two series of compounds: (1) *arsenious*, in which it is trivalent; and (2) *arsenic*, in which it is pentavalent. Its hydroxides are amphoteric, so that it forms cations and anions in both series.

Cations	Anions
Arsenious, As ⁺⁺⁺	Arsenite (meta), AsO ₂ ⁻
	Arsenite (ortho), AsO ₃ ⁻⁻⁻
Arsenic, As ⁺⁺⁺⁺⁺	Arsenate (meta), AsO ₃ ⁻
	Arsenate (ortho), AsO ₄ ⁻⁻⁻

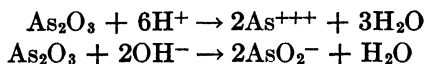
The arsenic ion As⁺⁺⁺⁺⁺ is never present in solution in more than traces, owing to its reaction with water, forming arsenic acid, H₃AsO₄.

Arsenious Compounds

Solubilities.—The only important salt of the As⁺⁺⁺ ion is the trichloride, AsCl₃. Its solution in HCl is the stock solution for

the As^{+++} ion. The arsenites of sodium and potassium are soluble; the others are generally insoluble.

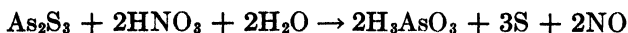
Arsenious Oxide.—The starting material for all arsenious compounds is arsenic trioxide, a by-product in the roasting arseniferous ores. It is amphoteric, dissolving in HCl to form arsenious ions and in NaOH to form arsenite ions.



As_2O_3 is the "white arsenic" of commerce, and its principal industrial importance is the manufacture of insecticides and fungicides.

Arsenic Trichloride.— AsCl_3 is a colorless liquid, boiling at 130° . Since it dissolves in water with partial hydrolysis, dilute HCl is used as the solvent. Owing to its volatility, it may be completely removed from solution by boiling. This is the basis of a quantitative method for separating arsenic.

Arsenic Trisulfide.—When AsCl_3 solution is saturated with H_2S , a yellow precipitate of As_2S_3 is rapidly obtained, thus: $2\text{As}^{+++} + 3\text{H}_2\text{S} \rightarrow \text{As}_2\text{S}_3 + 6\text{H}^+$. As_2S_3 is exceedingly insoluble; it may be completely precipitated in the presence of concentrated HCl . On the other hand, it is slowly soluble in concentrated HCl on prolonged boiling. It is soluble in dilute HNO_3 , forming a number of oxidation products. The main reaction may be considered to be



However, the H_3AsO_3 may be more or less oxidized to H_3AsO_4 and the sulfur to H_2SO_4 , depending on conditions.

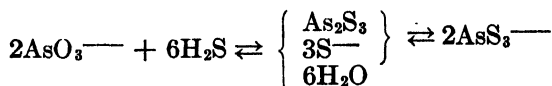
As_2S_3 dissolves readily in alkaline sulfides, such as $(\text{NH}_4)_2\text{S}$ or Na_2S , forming thioarsenites, thus: $\text{As}_2\text{S}_3 + 3\text{S}^{--} \rightarrow 2\text{AsS}_3^{--}$. If polysulfides are used, the excess sulfur oxidizes the arsenic to the pentavalent state, giving the thioarsenate, thus: $\text{As}_2\text{S}_3 + 3\text{S}^{--} + 2\text{S} \rightarrow 2\text{AsS}_4^{--}$. As_2S_3 is readily soluble in ammoniacal solutions, such as NH_4OH or $(\text{NH}_4)_2\text{CO}_3$, giving products whose composition is not definitely known. It is also soluble in NaOH solution, probably giving a mixture of AsS_3^{--} and AsO_3^{--} .



Arsenites.—The only soluble arsenite of importance is sodium arsenite, used industrially as an antiseptic and weed killer. It is formed by dissolving As_2O_3 in NaOH or Na_2CO_3 solution. A saturated solution of As_2O_3 in NaOH approximates the composition NaAsO_2 . The formation of the meta-arsenite is to be expected; for arsenious acid is a weak acid, with its ionization mainly that of the first H atom. Strongly alkaline solutions probably contain the orthoarsenite ion AsO_3^{--} .



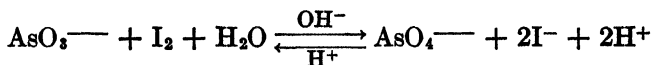
In neutral or alkaline solution, arsenites do not give a precipitate of As_2S_3 with H_2S . The arsenite ion may be considered to react with H_2S , forming first As_2S_3 and S^{--} ions; but these immediately react with each other, forming the thioarsenite ion. For example,



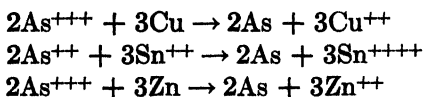
Silver arsenite, Ag_3AsO_3 , is a yellow salt, soluble in dilute HNO_3 and in NH_4OH .

Mg^{++} ions do not form a precipitate with AsO_3^{--} in the presence of NH_4OH and NH_4^+ ions (*cf.* the arsenate ion AsO_4^{--}).

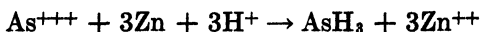
Oxidation and Reduction.—Trivalent arsenic compounds are oxidized to pentavalent forms by active oxidizing agents, such as HNO_3 or aqua regia. This oxidation proceeds more readily in alkaline than in acid medium. For example, I_2 oxidizes AsO_3^{--} in alkaline solution but not As^{+++} in acid solution. On the other hand, in acid solution AsO_4^{--} is reduced by HI to AsO_3^{--} . These reactions may be represented thus:



Strong reducing agents reduce As^{+++} to metallic arsenic.



By reason of its high reducing power, zinc reduces As^{+++} to arsine to a greater or less extent.



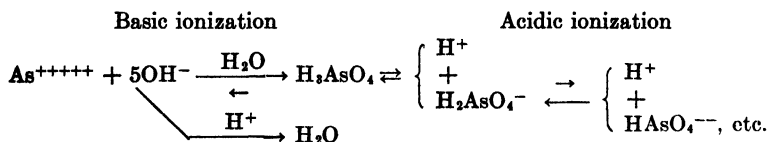
See Marsh and Gutzzeit tests, pages 214 to 216.

Arsenic Compounds

Pentavalent arsenic is nonmetallic in nature, appearing almost wholly in the anion form.

Solubilities.—The soluble arsenates are arsenic acid and sodium, potassium, and ammonium arsenates. All others are insoluble in water, but soluble in acids.

Arsenic Acid.—Arsenic acid, H_3AsO_4 , is a white crystalline solid, fairly soluble in water. Its solution is a weak acid, forming, in the absence of a strong base, mainly primary arsenate ions H_2AsO_4^- . H_3AsO_4 has basic properties, though to a very small extent.

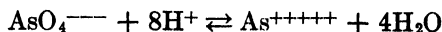


These equilibriums may be displaced to the left by adding a high concentration of H^+ ions. These ions both repress the acid ionization and increase the basic ionization by the removal of OH^- ions.

Arsenic Pentasulfide.—When a solution of H_3AsO_4 is saturated with H_2S , yellow As_2S_5 is precipitated. This precipitation proceeds slowly—much more slowly than the precipitation of As_2S_3 from H_3AsO_3 . This slow reaction is explained by the exceedingly low concentration of As^{+++++} ions in the solution. The formation of As_2S_5 may be favored by increasing the concentration of (1) the As^{+++++} or (2) the S^- ions. The concentration of As^{+++++} can be increased only by increasing the concentration of the H^+ , but that in turn represses the concentration of the S^- ions. However, these effects are not equal; the gain in As^{+++++} ions more than compensates for the loss in S^- ions.

This favorable effect of acidity upon the precipitation of As_2S_5 from AsO_4^{--} solution may be explained as follows: The equation for the formation of As_2S_5 is $2\text{As}^{+++++} + 5\text{S}^- \rightarrow \text{As}_2\text{S}_5$. As

shown on page 46, the forward speed in this reaction is $\vec{S} = k_1[\text{As}^{+++++}]^2[\text{S}^-]^5$. The equations for the formation of As^{+++++} and S^- are



and



Applying the mass law,

$$\frac{[\text{As}^{+++++}]}{[\text{AsO}_4^{---}][\text{H}^+]^8} = k_2$$

and

$$\frac{[\text{H}^+]^2[\text{S}^{--}]}{[\text{H}_2\text{S}]} = k_3$$

Solving for $[\text{As}^{+++++}]$ and $[\text{S}^{--}]$,

$$\begin{aligned} [\text{As}^{+++++}] &= k_2[\text{AsO}_4^{---}][\text{H}^+]^8 \\ [\text{S}^{--}] &= k_3 \frac{[\text{H}_2\text{S}]}{[\text{H}^+]^2} \end{aligned}$$

Substituting these values in $\vec{S} = k_1[\text{As}^{+++++}]^2[\text{S}^-]^5$,

$$\vec{S} = k_1 \times k_2^2 [\text{AsO}_4^{---}]^2 [\text{H}^+]^{16} \times k_3^5 \frac{[\text{H}_2\text{S}]^5}{[\text{H}^+]^{10}}$$

or,

$$\vec{S} = k_1 k_2^2 k_3^5 [\text{AsO}_4^{---}]^2 [\text{H}_2\text{S}]^5 [\text{H}^+]^6$$

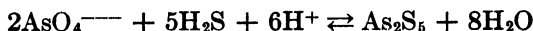
All of the quantities on the right side of the last equation are constants or fixed, except $[\text{H}^+]^6$. k_1 , k_2 , k_3 are equilibrium constants, $[\text{AsO}_4^{---}]$ is fixed by the amount of the arsenate present in the solution, and $[\text{H}_2\text{S}]$ is the solubility of H_2S in water. All of these factors may then be combined in a single constant k_4 .

$$\vec{S} = k_4 [\text{H}^+]^6$$

That is, the speed of formation is proportional to the sixth power of the concentration of the H^+ ions. It follows that the highest possible concentration of H^+ is desirable, and so concentrated

HCl (16 molar) is used. Experiment confirms the validity of this kinetic treatment.

The same result may be obtained by applying the mass law to the over-all equation



In this case,

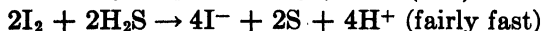
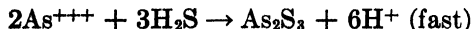
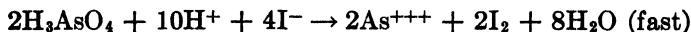
$$\vec{S} = k[\text{AsO}_4\text{---}]^2 \times [\text{H}_2\text{S}]^5 \times [\text{H}^+]^6$$

As before, $[\text{AsO}_4\text{---}]$ and $[\text{H}_2\text{S}]$ are fixed, so that

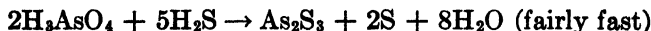
$$\vec{S} = \text{constant} \times [\text{H}^+]^6$$

Slow reactions may be speeded up by increase in temperature. It was pointed out long ago that the speed of the average reaction is doubled, sometimes tripled, for each 10° increase in temperature. This would mean that the precipitation of As_2S_5 should proceed 2^7 (i.e., 128) times as fast at 100° as at 30° . Precipitation from hot solution does accelerate the precipitation of As_2S_5 , though perhaps not 128 times.

Another procedure for speeding up slow reactions is the substitution of fast reactions for slow ones. In this case, the precipitation may be hastened by adding I^- to the reaction mixture. H_3AsO_4 is rapidly reduced to As^{+++} by HI , and As^{+++} ions are rapidly precipitated as As_2S_3 by H_2S . At the same time, H_2S reduces the I_2 formed in the first step back to I^- .

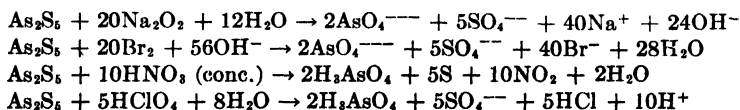


Adding,



Two things should be noted: (1) The I^- ion is regenerated. Consequently a small amount of I^- is sufficient for any reaction. (2) The final precipitate is not As_2S_5 but $\text{As}_2\text{S}_3 + 2\text{S}$, which is equivalent to it. The I^- may be considered a catalyst, since it speeds up the reaction and yet can be recovered in the end unchanged in amount.

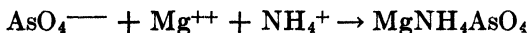
Arsenic pentasulfide shows the same solubility effects as As_2S_3 . It is soluble in alkaline sulfides, such as $(\text{NH}_4)_2\text{S}$ or Na_2S , forming the thioarsenate anion: $\text{As}_2\text{S}_5 + 3\text{S}^{--} \rightleftharpoons 2\text{AsS}_4^{--}$. It is soluble in NaOH , possibly forming a mixture of AsS_4^{--} and AsO_4^{--} . It is soluble in NH_4OH and $(\text{NH}_4)_2\text{CO}_3$, forming undetermined products. It is soluble in oxidizing agents; *e.g.*,



The first two equations are exact. The last two are approximate, not including certain minor products that are present in variable amounts, *e.g.*, SO_2 , NO , Cl_2 , ClO_2 , etc.

Insoluble Arsenates.—Of the large number of insoluble arsenates, two are of particular analytical interest.

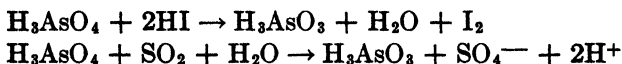
Magnesium Ammonium Arsenate.—This is a white crystalline salt, precipitated by the reaction between AsO_4^{--} ions and “magnesia mixture” [a solution containing an Mg^{++} salt, NH_4OH , and enough of an NH_4^+ salt to prevent the precipitation of $\text{Mg}(\text{OH})_2$].



Silver Arsenate.— AsO_4^{--} is precipitated by Ag^+ ions from neutral solutions as a chocolate-brown precipitate. This salt is more insoluble than $\text{MgNH}_4\text{AsO}_4$. Consequently, Ag^+ ions convert $\text{MgNH}_4\text{AsO}_4$ into Ag_3AsO_4 .



Reduction of Arsenates.—Active acidic reducing agents reduce H_3AsO_4 to H_3AsO_3 ; *e.g.*,



Arsenates are not readily reducible in alkaline solution. This suggests that AsO_4^{--} is more stable than H_3AsO_4 .

Detection.—Outside of the exceedingly sensitive micro tests (see the following paragraphs) used in toxicological work, the most important procedure in the detection of arsenic is (1) its

precipitation as white $\text{MgNH}_4\text{AsO}_4$, and (2) the conversion of this product into brown Ag_3AsO_4 . AsO_3 — is not precipitated by magnesia mixture and must be oxidized to AsO_4 — before the procedure already described may be applied.

MICRO TESTS

Arsenic is the best known of the mineral poisons. It was the main resource of the professional poisoners of the Middle Ages, and its homicidal use has continued even up to the present time. Tardieu has made a study (Table 24) of the homicides by poisoning in France for the period 1851–1871 and found that more than 33 per cent were due to arsenic and 30 per cent were due to phos-

TABLE 24.—RELATIVE USE OF POISONS IN HOMICIDES IN FRANCE FOR 1851–1871

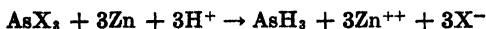
Arsenicals.....	331	Opiates.....	12
Phosphorus.....	301	Mercury compounds.....	9
Copper compounds.....	183	Antimony compounds.....	6
Mineral acids.....	54	Cyanides.....	5
Cantharides.....	35	Iron compounds.....	5
Strychnine.....	14		

phorus (rat poison), whereas the commonest of the organic poisons rank from 1 to 3.5 per cent.

During the last half century, there has been a notable diminution in the use of arsenic for homicidal purposes. This is largely due to the certainty of the tests used for detecting this element. The clever criminal now turns to agencies not so easily traced—bacteria and toxins, for example.

Marsh Test.—The first of the very sensitive tests for arsenic was the Marsh test (1836). The principle of this procedure is (1) the reduction of the arsenic compound to arsine, AsH_3 , and (2) the decomposition of the arsine by heat, forming a black glossy stain ("mirror") of metallic arsenic.

The material to be tested is placed in a hydrogen generator containing zinc and hydrochloric or dilute sulfuric acid, which reduces the arsenic to arsine.



The arsine is passed through a hard glass tube (Fig. 27) with one or more

constrictions. This tube is heated just in front of a constriction, decomposing the arsine into metallic arsenic and hydrogen.

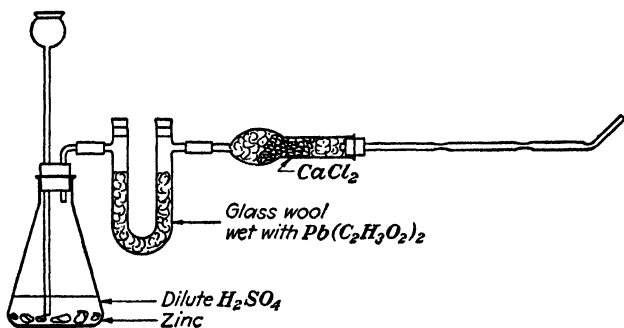
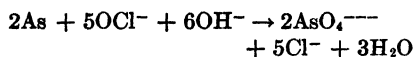


FIG. 27.—The Marsh test for arsenic.

The arsenic vapor condenses in the narrow part of the tube as a black glossy deposit. Antimony compounds give similar results, but the arsenic deposit may be distinguished by its solubility in NaOCl solution.



This test is exceedingly sensitive; as little as 0.002 mg. of arsenic may be detected. The amount of arsenic may be quantitatively estimated by comparing the deposit with stains from known amounts of arsenic.

Fleitmann's Test.—Fleitmann (1851) modified the Marsh test by using metallic aluminum and sodium hydroxide solution instead of the zinc and acid. This avoids the interference by antimony. On the other hand, the sensitivity of the test is not so high as that of the Marsh test. Further, arsenates must previously be reduced to trivalent arsenious compounds.

The Gutzeit Test.—The preceding tests have now been superseded by the Gutzeit test (1879), which has the advantage of

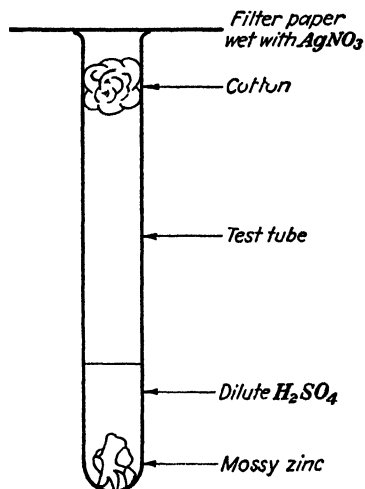
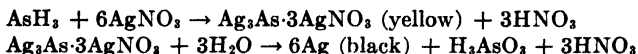


FIG. 28.—The Gutzeit test for arsenic.

simpler apparatus and freedom from the dangerous explosions that occur when air is not completely displaced from the hydrogen generator.

An ordinary test tube (Fig. 28) is used as a generator for the arsine. Pure zinc, dilute H_2SO_4 , a little CuSO_4 to act as a catalyst, and the unknown are introduced into the tube. A plug of cotton moistened with $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ to stop any spray and to absorb H_2S is inserted in the top of the tube. The tube is covered with a piece of filter paper bearing a crystal of AgNO_3 or moistened with a solution of that salt. If arsenic is present, the paper turns first yellow, then black.



In the modified Gutzeit test (Fig. 29), strips of paper containing HgCl_2 are used to detect the arsine.



The sensitiveness of this test is variously estimated. It is hardly so delicate as the Marsh test, though some have claimed that it will detect as little as 0.0001 mg. of arsenic.

The Hoffmann Test.—In this test, the arsine is absorbed in a solution of AgNO_3 , giving a precipitate of black silver. The equation for the reaction is the same as the one given under the Gutzeit test. Antimony interferes with the test by forming black silver antimonide, Ag_3Sb . Arsenic can be differentiated from antimony by testing the filtrate for H_3AsO_3 , which gives with AgNO_3 in neutral solution a yellow precipitate of Ag_3AsO_3 . In the test with antimony, no analogous reaction is obtained. The test is made as follows.

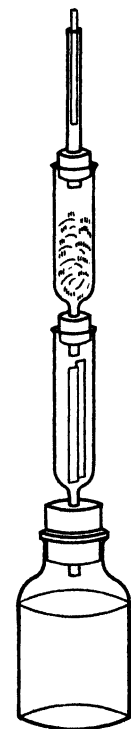
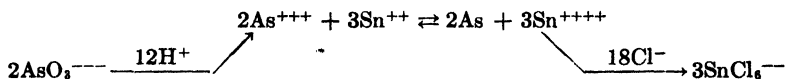


FIG. 29.—
The modified
Gutzeit test
for arsenic.

The black precipitate is removed by filtration, and a slight excess of AgNO_3 is added to the solution. By means of a thistle tube or pipette, a portion of the solution is introduced below some dilute NH_4OH . At the neutral junction between the acid and ammoniacal layers, a yellow "ring" of Ag_3AsO_3 forms.

The Bettendorff Test.—This test is based on the reduction of the arsenic compound to metallic arsenic by means of SnCl_2 . The procedure is as follows.

A small amount of the solution under examination is added to a solution of SnCl_2 in concentrated HCl , and the mixture warmed. A brown-to-black coloration is due to metallic arsenic. Mercury and silver compounds interfere by giving black precipitates of the metals. Antimony compounds do not interfere, for Sn^{++} ions do not reduce Sb^{+++} . The fundamental equation involved is $2\text{As}^{+++} + 3\text{Sn}^{++} \rightarrow 2\text{As} + 3\text{Sn}^{++++}$. The presence of concentrated HCl is necessary for two reasons: (1) The high concentration of H^+ increases the concentration of the As^{+++} ions: $\text{AsO}_3^{---} + 6\text{H}^+ \rightleftharpoons \text{As}^{+++} + 3\text{H}_2\text{O}$. (2) The excess of Cl^- ions ties up the Sn^{++++} as chlorostannate: $\text{Sn}^{++++} + 6\text{Cl}^- \rightleftharpoons \text{SnCl}_6^{--}$. The total equilibrium may be represented:



The Reinsch Test.—This test is based upon the displacement of As^{+++} by metallic copper, forming cupric arsenide, Cu_3As_2 . The test is carried out as follows.

The solution to be tested is strongly acidified with concentrated HCl , and a strip of bright copper foil is introduced. Upon boiling, the Cu_3As_2 forms upon the surface of the copper as a gray deposit. The test may be further confirmed by removing the Cu_3As_2 and gently igniting it in a dry test tube. The Cu_3As_2 is oxidized by the air: $\text{Cu}_3\text{As}_2 + 4\text{O}_2 \rightarrow 5\text{CuO} + \text{As}_2\text{O}_3$. The As_2O_3 sublimes, forming a white crystalline sublimate on the cooler part of the tube.

The ions of other elements below hydrogen in the e.m.f. series also form deposits on copper—*e.g.*, Ag , Hg , Sb , and Bi .

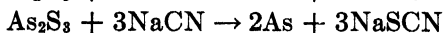
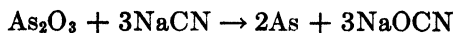
The Reinsch test is not so sensitive as the preceding tests. It was formerly extensively used in the detection of arsenicals used as green pigments in wallpapers, window shades, etc.

Cacodyl Oxide.—When a dry acetate is heated with As_2O_3 , gaseous cacodyl oxide, $[(\text{CH}_3)_2\text{As}]_2\text{O}$, is formed. Illustrating by sodium acetate,



This gas has a very foul odor and is extremely poisonous. The reaction is sensitive, but it is unsuitable for general laboratory work.

Reduction by Cyanides.—When As_2O_3 or As_2S_3 is fused in a hard glass tube with NaCN in the presence of excess Na_2CO_3 , the arsenic is reduced to the metallic state, and the cyanide is oxidized to a cyanate.



The arsenic forms a black mirror on the cooler part of the tube. Fresenius and Babo reported that as little as 0.01 mg. of arsenic would give a positive test.

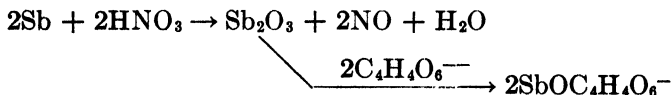
ANTIMONY

The Metal.—Antimony is a white, brittle metal, resembling bismuth in its physical properties. It is used in making alloys of low melting point, and particularly alloys that expand slightly upon solidification—printers' alloys, for example.

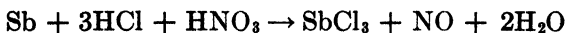
Antimony is not attacked by HCl or dilute H_2SO_4 . Concentrated HNO_3 oxidizes it to insoluble antimony tetroxide, Sb_2O_4 .



Dilute HNO_3 will dissolve it readily if some reagent is present that will dissolve the oxides of the metal, forming soluble complexes—*e.g.*, tartaric acid.



The best solvent for antimony is aqua regia.

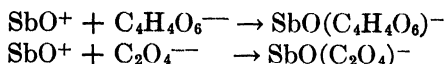


Ions.—Antimony forms two series of compounds: (1) *antimonious*, in which the element is trivalent; and (2) *antimonic*, in which it is pentavalent. Theoretically, antimony is amphoteric, forming cations and anions in both series. Certain of these ions are more or less hypothetical, existing only in small concentrations in equilibrium with complex ions. Such ions are designated by brackets in the following list:

Cations	Anions
Antimonious, Sb^{+++}	Antimonite (meta), SbO_3^-
Antimonyl, SbO^+	Antimonate (ortho), SbO_4^{---}
[Antimonic, Sb^{+++++}]	Antimonate (meta), SbO_3^-

Antimonious Compounds

Solubilities.—Owing to the formation of insoluble antimonyl compounds, the Sb^{+++} ion forms few soluble salts. In the presence of free acids, this hydrolysis is repressed, and clear solutions are obtained. SbCl_3 is soluble in this sense. Antimonyl salts containing inorganic anions are insoluble, *e.g.*, SbOCl . With certain organic anions, antimonyl ions form complex anions whose salts are soluble, *e.g.*, tartrates and oxalates.



The sulfide, Sb_2S_3 , and the hydroxide, $\text{Sb}(\text{OH})_3$, are the most important compounds.

Hydrolysis of Antimonious Ions.— Sb^{+++} ions react reversibly with water (hydrolysis), forming antimonyl ions SbO^+ , thus: $\text{Sb}^{+++} + \text{H}_2\text{O} \rightleftharpoons \text{SbO}^+ + 2\text{H}^+$. Antimonyl salts are variously named. For example, SbOCl is known as *antimonyl chloride*, *antimony oxychloride*, and *basic antimony chloride*.

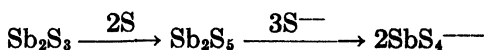
Antimonious nitrate and antimonious sulfate are almost completely hydrolyzed, and solutions of these salts cannot be prepared. The greater stability of SbCl_3 solutions is most easily explained by assuming that SbCl_3 is much less ionized than $\text{Sb}(\text{NO}_3)_3$ and therefore gives a lower concentration of Sb^{+++} ions to react with water. Probably SbCl_3 exists in HCl solution mainly as chloroantimonite anions SbCl_4^- .

Antimonyl precipitates are soluble in tartrates and oxalates, owing to the formation of complex ions. The most important commercial representative of antimonyl salts is potassium antimonyl tartrate (tartar emetic), $\text{KSbOC}_4\text{H}_4\text{O}_6$. It is used as a mordant in dyeing cloth and leather.

Hydroxide.—The Sb^{+++} ion is precipitated as white $\text{Sb}(\text{OH})_3$ (or SbOOH) by basic solutions, such as NaOH , NH_4OH , and Na_2CO_3 . Like $\text{As}(\text{OH})_3$, it is amphoteric. As antimony hydroxide, $\text{Sb}(\text{OH})_3$, it reacts with strong acids, forming the antimonious ion Sb^{+++} ; and as antimonious acid, H_3SbO_3 , it reacts with strong bases, forming the antimonite (meta) anion SbO_2^- .

Sulfide.— Sb^{+++} ions are precipitated by H_2S as orange Sb_2S_3 , soluble in concentrated HCl . Sb_2S_3 is not sufficiently acidic to

dissolve readily in colorless $(\text{NH}_4)_2\text{S}$. It is easily soluble in yellow $(\text{NH}_4)_2\text{S}_x$. The excess sulfur in the polysulfide oxidizes the Sb_2S_3 first to Sb_2S_5 , and that dissolves in $(\text{NH}_4)_2\text{S}$, forming the thioantimonate anion.



The thioantimonite ion SbS_3^{--} exists, if at all, in small amounts.

Upon prolonged boiling of a solution containing red Sb_2S_3 , the latter changes into a black form.

Reduction.— Sb^{+++} ions are displaced from solution by aluminum, iron, tin, etc., as black antimony. Zinc, by reason of its greater reducing action, reduces Sb^{+++} more or less to stibine, SbH_3 . Like AsH_3 , SbH_3 is decomposed by heat, forming a glossy black mirror.

Oxidation.—Antimonious compounds are oxidized to antimonie compounds by strong oxidizing agents. The reaction proceeds more readily in alkaline rather than acid medium.

Antimonic Compounds

Solubilities.—Antimony pentachloride, SbCl_5 , is soluble in concentrated HCl but hydrolyzes upon addition of water, forming white insoluble antimonie acid, H_3SbO_4 . The sulfide, Sb_2S_5 , is the most important insoluble compound.

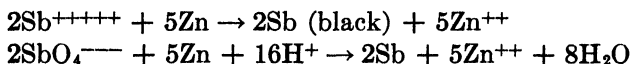
Ions.—The solution of SbCl_5 in HCl presumably contains some Sb^{+++++} ions. This is evidenced by its formation of Sb_2S_5 with H_2S . Three types of antimonates have been reported—ortho, pyro, and meta. These may be taken to indicate the existence of the corresponding anions SbO_4^{--} , $\text{Sb}_4\text{O}_7^{--}$, and SbO_3^- . The meta-antimonate ion SbO_3^- would be expected to be the most abundant.

Antimonic Acid.— H_3SbO_4 is a white solid, only slightly soluble in water. It is practically insoluble in HNO_3 and H_2SO_4 but dissolves in HCl , owing to the formation of a complex chloro-antimonate ion SbCl_6^- . It is soluble in tartrates, forming the complex anion $\text{SbO}_2(\text{C}_4\text{H}_4\text{O}_6)^-$, and in KOH solution, forming SbO_4^{--} (or SbO_3^-).

Antimonic Sulfide.— Sb_2S_5 is formed when SbCl_5 or $\text{SbO}_2\text{-(C}_4\text{H}_4\text{O}_6)^-$ solution is saturated with H_2S . It is an orange-red

solid, soluble in concentrated HCl. It also dissolves in alkaline sulfides— $(\text{NH}_4)_2\text{S}$ or Na_2S —forming the thioantimonate ion: $\text{Sb}_2\text{S}_5 + 3\text{S}^{--} \rightarrow 2\text{SbS}_4^{--}$. The sulfide is reprecipitated upon acidification, thus: $2\text{SbS}_4^{--} + 6\text{H}^+ \rightarrow \text{Sb}_2\text{S}_5 + 3\text{H}_2\text{S}$.

Reduction.—Iodine ions in acid solution reduce Sb^{++++} to Sb^{+++} : $\text{Sb}^{++++} + 2\text{I}^- \rightarrow \text{Sb}^{+++} + \text{I}_2$. Active metals, such as zinc, aluminum and iron, reduce it to the metallic form; *e.g.*,



Zinc, by reason of its stronger reducing power, takes some of the antimony to stibine, SbH_3 .

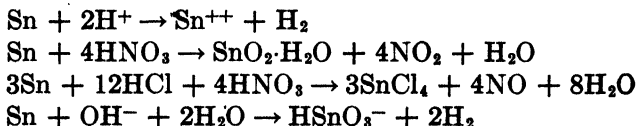


Detection.—The sulfides are the most distinctive compounds formed by antimony. Consequently all the tests are based upon the formation and solution of Sb_2S_3 and Sb_2S_5 .

TIN

The Metal.—Tin is a soft, white metal, untarnished by air. It is used in “tinning” sheet iron and in a number of important alloys, such as solder, Babbitt metal, and bronzes.

Tin dissolves slowly in cold dilute HCl but readily in hot concentrated HCl, forming stannous chloride, SnCl_2 . Concentrated HNO_3 does not dissolve it but converts it into a white hydrated oxide, $\text{SnO}_2 \cdot \text{H}_2\text{O}$, known as *metastannic acid*. Aqua regia dissolves tin readily, forming SnCl_4 (or H_2SnCl_6). It is slowly dissolved by hot NaOH and KOH solutions, forming stannates. Equations for the above reactions are as follows:



Ions.—Tin forms two series of compounds: (1) *stannous*, in which the element is bivalent, and (2) *stannic*, in which it is tetravalent. The hydroxides are amphoteric, forming both cations and anions. The stannic ion Sn^{++++} must be considered more or less hypothetical, since an HCl solution of SnCl_4 contains

tin mainly in the form of chlorostannate anions SnCl_6^{--} . It is assumed that this ion dissociates to some extent into Sn^{++++} . This is indicated by the precipitation of SnS_2 by H_2S . This ion is therefore indicated by brackets.

Cations	Anions
Stannous, Sn^{++}	Stannite, HSnO_2^-
[Stannic, Sn^{++++}]	Stannate (meta), HSnO_3^-
	Chlorostannate, SnCl_6^{--}

Stannous Compounds

Stannous Chloride.—The most important of the soluble stannous salts is the chloride, SnCl_2 , used industrially as a mordant in dyeing. Stannous hydroxide is a weak base, and consequently Sn^{++} solutions tend to hydrolyze, forming basic salts, which are usually insoluble—*e.g.*, $\text{Sn}(\text{OH})\text{Cl}$. Dilute HCl is therefore used as a solvent in preparing SnCl_2 solutions. A small amount of metallic tin is usually added to reduce any Sn^{++++} ions formed by atmospheric oxidation back to the Sn^{++} form: $\text{Sn}^{++++} + \text{Sn} \rightarrow 2\text{Sn}^{++}$ (see page 150).

Stannous Hydroxide.— Sn^{++} ions react with moderate concentrations of OH^- ions, forming white $\text{Sn}(\text{OH})_2$. Na_2CO_3 and NH_4OH give sufficient OH^- ions for this reaction. $\text{Sn}(\text{OH})_2$ is amphoteric, dissolving in both strong acids and strong bases. Its dual ionization may be represented:



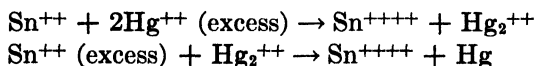
Strong acids give this equilibrium a leftward shift by removing the OH^- ions by means of H^+ , and strong bases favor the rightward reaction by removing the H^+ ions by means of OH^- . The formula of the stannite ion is usually written SnO_2^{--} ; however, HSnO_2^- seems more probable, for acids as weak as H_2SnO_2 are not expected to ionize beyond the first H atom.

Stannous Sulfide.—This is the most important of the insoluble stannous compounds. It is formed as a brown precipitate SnS when an Sn^{++} solution is saturated with H_2S . It is soluble in moderate concentrations of HCl ; therefore, the acidity must be low (not over 0.3 *M* H^+) for Sn^{++} to be completely precipitated.

It seems to have no acidic properties, for it is insoluble in $(\text{NH}_4)_2\text{S}$ and Na_2S solutions. It does dissolve in yellow $(\text{NH}_4)_2\text{S}_x$.

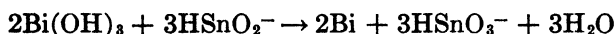
or Na_2S_x , owing to oxidation to SnS_2 by the "polysulfide sulfur" (see page 227).

Reducing Action.—The most conspicuous property of the Sn^{++} ion is its strong reducing action. It reduces the cations of all the metals below bismuth in the e.m.f. series (page 150) to the metallic state; e.g., $\text{Cu}^{++} + \text{Sn}^{++} \rightarrow \text{Cu} + \text{Sn}^{++++}$. Sn^{++} reduces Hg^{++} ions in steps, first to Hg_2^{++} , and later to Hg .

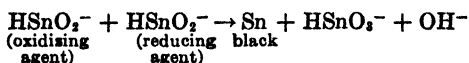


If Cl^- ions are present, the Hg_2^{++} passes through the Hg_2Cl_2 form. This reducing action of the Sn^{++} ion is accentuated by the presence of an excess of Cl^- ions, which tend to remove the Sn^{++++} ions as SnCl_6^{--} (see page 221), thereby giving the reaction an additional forward stress.

The stannite ion appears to be an even stronger reducing agent than the Sn^{++} , reducing bismuth hydroxide to black metallic bismuth.



Certain precautions must be taken in preparing sodium stannite solution. NaOH solution is added to SnCl_2 solution slowly, with shaking, until the solution contains a permanent precipitate of white $\text{Sn}(\text{OH})_2$, and then more NaOH is added in sufficient quantity to give a clear solution. This mixture will be strongly basic. The reagent is prepared from diluted reagents, since hot concentrated solution of Na_2SnO_2 may undergo autooxidation and reduction, forming black metallic tin.



Stannic Compounds

The chemistry of stannic compounds is involved for two reasons: (1) the high insolubility of the hydroxides favors the hydrolysis of the soluble salts; and (2) tin has a tendency to form complex ions of various types.

Stannic Chloride.—This is the most important of the soluble stannic salts. In the pure form, it is a clear fuming liquid. Upon adding water, a white precipitate is formed, containing hydrates of SnCl_4 and stannic hydroxide. A solution may be obtained by using HCl solution as the solvent. The solution contains mainly chlorostannic acid and its ions.



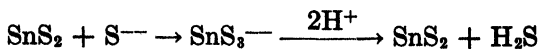
Several chlorostannates are known in the solid form; *e.g.*, the "pink salt" used in the textile industry as a mordant for red dyes is ammonium chlorostannate, $(\text{NH}_4)_2\text{SnCl}_6$. The SnCl_6^{--} ion seems to dissociate to a small degree into Sn^{++++} and Cl^- ions.

Stannic Hydroxides.— $\text{Sn}(\text{OH})_4$ is amphoteric, reacting with both strong acids and strong bases. The importance of its acidic properties has led to its being called *stannic acid*, and its formula is variously written $\text{Sn}(\text{OH})_4$, H_2SnO_3 , $\text{SnO}_2 \cdot x\text{H}_2\text{O}$, etc.

There are two forms of stannic acid, having different sets of properties. The $\text{Sn}(\text{OH})_4$ precipitated from Sn^{++++} solutions by means of bases is known as α (alpha) stannic acid or orthostannic acid. It is a white, gelatinous solid, soluble in HCl , forming chlorostannic acid, and in strong bases, forming soluble stannates. Upon standing or boiling, the α or orthostannic hydroxide goes over into the β (beta) or metastannic hydroxide. The β form may also be prepared by the action of concentrated HNO_3 on metallic tin. $\alpha\text{-Sn}(\text{OH})_4$ differs from $\beta\text{-Sn}(\text{OH})_4$ by being insoluble in dilute HNO_3 and dilute H_2SO_4 . Hot concentrated H_2SO_4 dissolves it, and the solution upon dilution gives $\alpha\text{-Sn}(\text{OH})_4$. Dilute HCl dissolves $\beta\text{-Sn}(\text{OH})_4$, reprecipitated by excess concentrated HCl . Evaporation of the HCl solution to dryness gives $\alpha\text{-Sn}(\text{OH})_4$.

Stannic Sulfide.— H_2S precipitates from Sn^{++++} solutions yellow SnS_2 , soluble in moderate concentrations of HCl . It is decomposed by hot HNO_3 , forming metastannic acid, sulfur, etc.

$\text{SnS}_2 + 4\text{HNO}_3 + x\text{H}_2\text{O} \rightarrow \text{SnO}_2 \cdot x\text{H}_2\text{O} + 2\text{S} + 4\text{NO}_2 + 2\text{H}_2\text{O}$
It is soluble in $(\text{NH}_4)_2\text{S}$, forming the thiostannate anion, and is reprecipitated upon acidification.



Reduction.—The reduction product of Sn^{++++} ions depends upon the strength of the reducing agent. Iron, lead, antimony, and copper reduce them to Sn^{++} ions; more active metals reduce them to metallic tin.

Detection.—Tin is detected by converting it into the Sn^{++} form and noting the reducing action of this ion on various

reagents: Sn^{++} ions give (1) with HgCl_2 , a white precipitate of Hg_2Cl_2 mixed with gray mercury; (2) with $(\text{NH}_4)_2\text{MoO}_4$ in the presence of HCl , a blue solution; (3) with $\text{Bi}(\text{OH})_3$ in the presence of excess NaOH , a black precipitate. A flaming test is described on page 424.

ANALYTICAL PROCEDURES

Regulation of Acidity.—Usually an excess of acid is used in dissolving materials for analysis. As a result, the acidity of the solution coming into Group II is too high for the complete precipitation of the more soluble sulfides of the group—particularly CdS , PbS , and SnS . It must be adjusted to a value that will permit the complete precipitation of Group II and yet will hold in solution the most insoluble sulfides of Group III. Experiment has led to the choice of $0.24\text{ }M\text{ H}^+$ (4 cc. of $6\text{ }M\text{ HCl}$ in 100 cc. of solution) as a good working value for this acidity.

The following procedures have been proposed for the adjustment of acidity.

1. *Dilution.*—Water is added to the solution until the desired acidity is shown by the proper indicator. The most suitable indicator for this purpose is methyl violet, the pigment sometimes used in the so-called “indelible” pencils. A series of scratches are made with such a pencil on glazed (not filter) paper, and dilution of the solution is continued until a drop of the solution no longer gives a yellow, but a greenish tint to the indicator. A blue color indicates too high a dilution. The indicator must not be added to the solution, since it is decomposed by the solution.

This procedure is objectionable for several reasons: (1) It may lead to unduly large volumes of solutions. (2) In many cases (*e.g.*, the presence of the ions of weak acids, such as $\text{HC}_2\text{H}_3\text{O}_2$), the color changes are too gradual to be satisfactory. (3) It does not remove organic matter and other substances that cause interference in Group III.

2. *Neutralization, Followed by Acidification.*—An indicator (*e.g.*, phenolphthalein) is added to the solution, and then NH_4OH is slowly added until the neutral tint appears. Four cubic centimeters of $6\text{ }M\text{ HCl}$ is then added, and the solution diluted to the proper volume.

There are several objections to this procedure: (1) The presence of a large amount of NH_4^+ salts interferes with subsequent work, particularly the precipitation of Group IV. (2) Organic matter and the anions of weak acids are not removed. (3) The added indicator may mask certain reactions in Group III.

3. *Evaporation of Free Acid, Followed by Reacidification.*—The solution is strongly acidified with HNO_3 and evaporated to a paste. The residue is then taken up in 4 cc. of 6 *M* HCl and diluted to the proper volume.

Besides being free from the objections to the two foregoing methods, the evaporation with HNO_3 serves several purposes: (1) It oxidizes all the Group II cations to their highest valences, thereby obviating the need for a large amount of $(\text{NH}_4)_2\text{S}_x$ or Na_2S_x in separating the subgroups. (2) It transposes volatile HgCl_2 and AsCl_3 into nonvolatile $\text{Hg}(\text{NO}_3)_2$ and H_3AsO_4 , respectively; otherwise these elements might be lost during the evaporation. (3) It displaces any anions of weak acids that might be present. As shown under buffer action (page 88), solutions containing the anions of weak acids cannot be acidified. For example, ZnS would be precipitated in Group II if $\text{C}_2\text{H}_3\text{O}_2^-$ were not previously removed. (4) It oxidizes organic matter, such as tartrates and sugars, that prevent the precipitation of the trivalent hydroxides in Group III. (5) Borates and fluorides are volatilized. If not removed at this point, they cause trouble by precipitating Group IV ions in Group III.

Precipitation of Group II.—The precipitation of Group II is best carried out in two stages: (1) The solution is diluted to 40 cc., heated to boiling, and saturated with H_2S . (2) It is then cooled, diluted to 100 cc., and again saturated with H_2S . The purpose of the first treatment is the precipitation of those sulfides which form best in hot, acidified solutions—*e.g.*, As_2S_5 . The precipitates obtained in this way are easier to filter and wash. The second precipitation takes care of the more soluble sulfides, like SnS and PbS , which are not completely thrown down in hot, concentrated solution.

The sulfides are precipitated, not simultaneously, but in the order in which their solubility products are exceeded. The precipitates form in about the following order: As_2S_5 , HgS , CuS , Sb_2S_3 , Bi_2S_3 , SnS_2 , CdS , PbS , and SnS .

In the event the H_2S treatment is stopped before precipitation is complete, the more soluble sulfides—particularly SnS and PbS , and maybe CdS —will not be precipitated. This may cause a double error: missing these elements in Group II, and spurious tests for elements in Group III that are really absent.

Arsenic in the form of AsO_4^{3-} is usually the most difficult member to precipitate. The most favorable conditions for the precipitation of As_2S_5 were shown on page 210 to be heat, presence of concentrated HCl , and the aid of a catalyst. In cases of turbid filtrates which give precipitates upon standing or upon resaturation with H_2S , AsO_4^{3-} is indicated. It should be remembered that the AsO_4^{3-} ion must be completely removed to avoid complications in Group III.

Division into Subgroups.—Group II is divided into two subgroups, generally known as the *Copper* and *Tin subgroups*. The reagent generally used in separating these groups is ammonium polysulfide, $(\text{NH}_4)_2\text{S}_x$. Owing to its oxidizing action, all the members of the group are oxidized to their highest valences. This reagent takes into solution the amphoteric sulfides— As_2S_5 , Sb_2S_5 , and SnS_2 —in the form of complex thio anions (*cf.* pages 115 to 116).

Certain procedures use sodium polysulfide, Na_2S_x , as the subgroup reagent, instead of $(\text{NH}_4)_2\text{S}_x$. In addition to As_2S_5 , Sb_2S_5 , and SnS_2 , this reagent dissolves HgS . The Tin subgroup procedure must be slightly modified so as to include Hg^{++} ions.

Solution of Sulfides in 2 M HNO_3 .—All sulfides except the most insoluble (HgS and As_2S_5) dissolve in boiling 2 M HNO_3 . A certain solubility in water (about 10^{-20} mole per liter for the sulfides of the divalent cations) is prerequisite to this solubility.

The sulfur that separates when sulfides dissolve in dilute HNO_3 is usually discolored, owing to flecks of brown or black sulfides being included in the sulfur particles. This impure sulfur may be distinguished from HgS by its floating in the hot acid. Bubbles of steam (probably containing a little NO and SO_2) adhere to the sulfur particles and float them to the top of the solution. HgS is too heavy to be floated in this way.

Solution of HgS in Aqua Regia.—Unnecessary amounts of aqua regia should be avoided in dissolving HgS , for such an excess protects HgCl_2 from reduction by SnCl_2 . Since aqua regia is

easier to reduce than HgCl_2 , the latter is not affected until all the aqua regia has been used up.

The boiling of the HgCl_2 solution in aqua regia should not be prolonged, for HgCl_2 is volatile in steam.

Removal of NO_3^- Ions.—The solution is evaporated with H_2SO_4 to expel the NO_3^- ions, which exert a solvent action on PbSO_4 (see page 192). The end point in this reaction is the formation of heavy white fumes of SO_3 which cause coughing. HNO_3 fumes are also white and may tempt the student to cough. But the urge is not so irresistible as with SO_3 . No more humane test has been found.

Hydrolysis of $\text{Pb}(\text{HSO}_4)_2$.—Upon dilution of the solution of PbSO_4 in concentrated H_2SO_4 , white microcrystals of PbSO_4 are formed (see page 193).

The hot H_2SO_4 is cooled and poured into water—not water into H_2SO_4 . The steam formed when water is added to concentrated H_2SO_4 may cause dangerous spattering. When the acid is poured into the water, the heat effects are not so marked. Water has a much higher specific heat than H_2SO_4 and absorbs the heat liberated by the hydration of H_2SO_4 without reaching the boiling point.

Separation of PbSO_4 from $(\text{BiO})_2\text{SO}_4$.—When Bi^{+++} is present in large amount, bismuthyl sulfate, $(\text{BiO})_2\text{SO}_4$, may separate upon dilution of the H_2SO_4 solution. PbSO_4 may be separated from $(\text{BiO})_2\text{SO}_4$ in several ways. The $(\text{BiO})_2\text{SO}_4$ may be washed out with dilute H_2SO_4 , or the PbSO_4 may be extracted by $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution. Better than either, the PbSO_4 may be extracted with NaOH solution. PbSO_4 dissolves readily in NaOH solution, forming HPbO_2^- anions, whereas the $(\text{BiO})_2\text{SO}_4$ is converted into insoluble $\text{Bi}(\text{OH})_3$. $\text{Bi}(\text{OH})_3$ is not acidic enough to dissolve in dilute bases. The Pb in HPbO_2^- may be detected by acidifying with $\text{HC}_2\text{H}_3\text{O}_2$ and adding $\text{K}_2\text{Cr}_2\text{O}_7$. Yellow PbCrO_4 will be precipitated. When $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ is used, the separation is not clean. A small amount of $(\text{BiO})_2\text{SO}_4$ is dissolved; and, when $\text{K}_2\text{Cr}_2\text{O}_7$ is added, a small precipitate may be due to yellow $(\text{BiO})_2\text{Cr}_2\text{O}_7$. This is soluble in $\text{HC}_2\text{H}_3\text{O}_2$, whereas PbCrO_4 is insoluble.

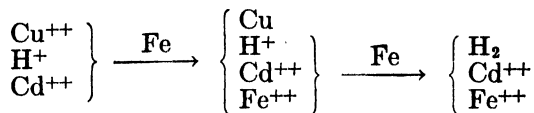
Reduction of $\text{Bi}(\text{OH})_3$ by Sodium Stannite.—Ordinarily, in testing for Bi^{+++} , the white precipitate with NH_4OH needs no

confirmation. Sometimes, when through careless technique all the Pb^{++} has not been removed, basic lead salts may form at this point. It may therefore be advisable to confirm the test for $\text{Bi}(\text{OH})_3$ by adding Na_2SnO_2 solution and precipitating black bismuth.

Care should be taken in making up Na_2SnO_2 solution. (1) It should be made up of diluted solutions, (2) the solutions should be cold, and (3) the mixture must be strongly alkaline. Concentrated and hot Na_2SnO_2 undergoes autoxidation reduction, giving black tin: $2\text{HSnO}_2^- \rightarrow \text{Sn} + \text{HSnO}_3^- + \text{H}_2\text{O}$ (cf. page 223).

Separation of Cd^{++} and Cu^{++} .—A number of procedures have been developed for separating Cd^{++} and Cu^{++} . The most important are the following.

1. *Displacement by Iron.*—If Fe (usually in the form of a nail) is placed in an acidified solution containing Cu^{++} and Cd^{++} , the following reactions occur in the order indicated:



After the copper and excess iron are filtered out, the solution is treated with H_2S , to precipitate CdS .

There are several objections to this procedure: (1) It is slow. If the Cu^{++} is not completely displaced, a black precipitate of CuS conceals any yellow CdS . (2) If the action is allowed to run too long, the free acid is exhausted, and then H_2S will give a black precipitate of FeS , which precipitates readily from neutral or very slightly acid solutions.

In case the precipitate is black, it is filtered out and warmed with dilute H_2SO_4 . CuS , Bi_2S_3 , etc., remain undissolved; PbS is changed into insoluble PbSO_4 ; and CdS and FeS dissolve. After having been cool and diluted, the solution is saturated with H_2S , when only yellow CdS can form.

2. *Complexing Copper Ions with CN^- .*—When NaCN solution is added to a Cu^{++} solution, the blue color disappears, and yellowish cupric cyanide, $\text{Cu}(\text{CN})_2$, is precipitated. This compound decomposes into white cuprous cyanide, $\text{Cu}_2(\text{CN})_2$, and cyanogen, C_2N_2 . The $\text{Cu}_2(\text{CN})_2$ dissolves in the excess CN^- ions, forming the complex cuprocyanide ion $\text{Cu}(\text{CN})_2^-$. This ion is very stable. Its dissociation into Cu_2^{++} and CN^- is so slight that H_2S will not

react with it. The corresponding $\text{Cd}(\text{CN})_4^-$ ion is not so stable and is completely decomposed by H_2S , precipitating yellow CdS .

When Cu^{++} is present in large amount, the ammoniacal solution contains considerable cyanogen, C_2N_2 . This reacts with H_2S , forming yellow-red crystals of dithiooxamide, $\text{H}_2\text{NCS}\cdot\text{SCNH}_2$, formerly called *hydrorubeanic acid*. This may be distinguished from CdS not only by its appearance but by its solubility in hot water.

3. *Precipitation of Cd^{++} as $\text{Cd}(\text{NH}_3)_4(\text{ClO}_4)_2$.*—A solution of NH_4ClO_4 in NH_4OH precipitates Cd^{++} as white $\text{Cd}(\text{NH}_3)_4(\text{ClO}_4)_2$, leaving copper in solution as the deep-blue $\text{Cu}(\text{NH}_3)_4^{++}$ ion. This precipitate forms slowly and is appreciably soluble in hot water. For these reasons, the mixture should stand for some time before filtering. The difficulty in this test for Cd^{++} is seeing the precipitate in the deep-blue solution of $\text{Cu}(\text{NH}_3)_4^{++}$ ions. This may be done more easily by filtering and washing the residue on the filter paper with a little concentrated NH_4OH .

4. *Precipitation of Cd^{++} as CdCO_3 .*—Karns¹ has proposed the following procedure: The ammoniacal filtrate from the $\text{Bi}(\text{OH})_3$ precipitation is mixed with 3 to 4 per cent NH_4Cl , and saturated NaHCO_3 is added. The Cd^{++} is precipitated as white CdCO_3 . The author reports that 1 mg. of Cd^{++} in 10 cc. of solution may be detected in this way.

Analysis of the Copper Subgroup.—With the exception of the step involving the separation of Cu^{++} and Cd^{++} , the procedures for the analysis of the Copper subgroup (Table 25) as given by most writers are practically identical.

Analysis of the Tin Subgroup.—In contrast to the unanimity of analysts as to the procedure for the analysis of the Copper subgroup, a number of schemes have been suggested for the Tin subgroup. This multiplication of procedures finds its explanation in the fact that none of those proposed is fully satisfactory and that analysts keep on trying to work out one that is. The following methods are most frequently used.

1. *Solubility of Sulfides in Graduated Concentrations of HCl .*—Professor A. A. Noyes has revived the procedure of separating the members of this subgroup on the basis of the solubilities of their sulfides in various concentrations of HCl . An outline of the method is shown in Table 26.

¹ *J. Am. Chem. Soc.*, **48**, 2626 (1926).

TABLE 25.—ANALYSIS OF THE COPPER SUBGROUP

$$\begin{array}{c}
 \left\{ \begin{array}{l} \underline{\text{HgS}} \\ \underline{\text{PbS}} \\ \underline{\text{Bi}_2\text{S}_3} \\ \underline{\text{CuS}} \\ \underline{\text{CdS}} \end{array} \right\} \xrightarrow[2\text{ M } \text{HNO}_3]{\text{boil}} \left\{ \begin{array}{l} \underline{\text{HgS}} \xrightarrow[\text{HNO}_3]{\text{HCl}} \xrightarrow{\text{HgCl}_2} \xrightarrow{\text{SnCl}_2} \xrightarrow{\text{Hg-Hg}_2\text{Cl}_2} \\ \text{Pb}^{++} \xrightarrow{\text{PbSO}_4} \xrightarrow{\text{NaOH}} \text{HPbO}_2^- \xrightarrow[\text{HAc}]{\text{K}_2\text{Cr}_2\text{O}_7} \text{PbCrO}_4 \\ \text{Bi}^{+++} \xrightarrow{\text{Bi}^{++}} \xrightarrow{\text{NH}_4\text{OH}} \left\{ \begin{array}{l} \text{Bi}^{++}, \text{Bi}(\text{OH})_3, \text{HSnO}_2^- \end{array} \right\} \xrightarrow{\text{Bi}} \text{Bi} \\ \text{Cu}^{++} \xrightarrow{\text{H}_2\text{SO}_4} \xrightarrow[\text{dilute}]{\text{evaporate,}} \left\{ \begin{array}{l} \text{Cu}^{++}, \text{Cu}(\text{NH}_3)_4^{++}, \text{Cd}(\text{NH}_3)_4^{++} \end{array} \right\} \xrightarrow[\text{H}_2\text{S}]{\text{NaCN,}} \left\{ \begin{array}{l} \text{Cu}(\text{CN})_2^- \\ \text{CdS} \end{array} \right\} \\ \text{Cd}^{++} \end{array} \right\}
 \end{array}$$

TABLE 26.—THE HCL METHOD

$$\begin{array}{c}
 \begin{array}{c}
 \text{As}_2\text{S}_5 \\
 \hline
 \text{S}
 \end{array}
 \xrightarrow[\text{HCl}]{\text{dilute}}
 \begin{array}{c}
 \text{As}_2\text{S}_5 \\
 \hline
 \text{Sb}_2\text{S}_5 \\
 \hline
 \text{SnS}_2 \\
 \hline
 \text{S}
 \end{array}
 \xrightarrow[\text{heat}]{\text{conc. HCl}}
 \begin{array}{c}
 \text{As}_2\text{S}_5 \\
 \hline
 \text{S}
 \end{array}
 \begin{array}{c}
 \xrightarrow{\text{HNO}_3, \text{ warm}} \\
 \xrightarrow{\text{dilute, H}_2\text{S}} \\
 \xrightarrow{\text{HgCl}_2}
 \end{array}
 \begin{array}{c}
 \text{H}_2\text{AsO}_4 \\
 \hline
 \text{H}_2\text{SO}_4
 \end{array}
 \begin{array}{c}
 \xrightarrow{\text{Mg(NO}_3)_2, \text{ NH}_4\text{OH}} \\
 \xrightarrow{\text{Sb}_2\text{S}_3} \\
 \xrightarrow{\text{Sn}^{++++}}
 \end{array}
 \begin{array}{c}
 \text{H}_2\text{AsO}_4 \\
 \hline
 \text{H}_2\text{SO}_4
 \end{array}
 \begin{array}{c}
 \xrightarrow{\text{Pb}} \\
 \xrightarrow{\text{AgNO}_3} \\
 \xrightarrow{\text{MgNH}_4\text{AsO}_4}
 \end{array}
 \begin{array}{c}
 \text{Pb} \\
 \hline
 \text{AgNO}_3 \\
 \hline
 \text{MgNH}_4\text{AsO}_4
 \end{array}
 \end{array}$$

2. *The Oxalic Acid Procedure.*—A procedure has been built on the quantitative procedures of F. W. Clarke and Levöl. Clarke separated As_2S_5 and Sb_2S_5 from Sn^{++++} by precipitation with H_2S in the presence of oxalic acid. Sn^{++++} ions combine with $\text{C}_2\text{O}_4^{--}$, presumably forming stannic oxalate, $\text{Sn}(\text{C}_2\text{O}_4)$, which is unaffected by H_2S . In the Levöl procedure, AsO_4^{--} is separated from SbO_4^{--} by precipitation by magnesia mixture as $\text{MgNH}_4\text{AsO}_4$. Tartrate or oxalate ions are added to prevent the precipitation of H_3SbO_4 . The procedure is outlined in Table 27.

3. *The Ammonium Carbonate Procedure.*—Another variant among the many procedures has been built upon the solubility of As_2S_5 in $(\text{NH}_4)_2\text{CO}_3$. Unfortunately, some Sb_2S_3 also dissolves, so that the separation is not clean. Usually, the Sb_2S_5 and SnS_2 in the residue are dissolved in concentrated HCl and separated by displacement with iron or other active metal.

4. *Displacement Reactions.*—Probably the most satisfactory procedure for testing for Sb^{+++} and Sn^{++++} in the presence of each other is by means of the zinc-platinum couple. A piece of zinc in contact with platinum foil is placed in the Sb^{+++} — Sn^{++++} solution. The Sb^{+++} deposits black antimony on the platinum, and the Sn^{++++} gray tin on the zinc. Each ion is deposited on the metal that opposes the least overvoltage. These deposits may be dissolved and tested for in the usual way.

The expensiveness of platinum has limited the use of this procedure. Silver coins work fairly well as a substitute for platinum, but care must be taken not to dissolve any of the coin in removing the antimony deposit. There are a number of other modifications in which other metals, such as iron, tin, and lead, are used to displace the Sb^{+++} .

Separation of Arsenic.—The following methods are used for the separation of arsenic from antimony and tin.

1. *Insolubility of As_2S_5 in Concentrated HCl .*— Sb_2S_5 and SnS_2 are soluble in hot 12 *M* HCl , whereas As_2S_5 is practically insoluble. With mixtures, the separation is never clean. Frequently, enough Sb_2S_5 remains to give the As_2S_5 an orange tint. Although As_2S_5 is very insoluble, the equilibrium $\text{As}_2\text{S}_5 + 10\text{HCl} + 3\text{H}_2\text{O} \rightleftharpoons 2\text{H}_3\text{AsO}_4 + 5\text{H}_2\text{S}$ may be slightly displaced to the right by allowing the mixture to boil, thereby removing H_2S . In quantitative work, the solution must be kept saturated with H_2S during heating to prevent loss of As_2S_5 .

2. *Solubility of As_2S_5 in $(\text{NH}_4)_2\text{CO}_3$.*—In a few procedures, as already stated, As_2S_5 is extracted with $(\text{NH}_4)_2\text{CO}_3$. The nature of the soluble product is not definitely known. The separation is not clean, for Sb_2S_5 is slightly soluble in $(\text{NH}_4)_2\text{CO}_3$ solution.

3. *Distillation of AsCl_3 .*—The most important of the quantitative methods for separating arsenic from antimony involves the distillation of AsCl_3 . The material containing the Tin subgroup is dissolved in concentrated HCl , and cuprous chloride, Cu_2Cl_2 , is added. Upon distillation, arsenic trichloride, AsCl_3 , passes over and is absorbed in NaOH or Na_2CO_3 solution. The temperature of the distillation is not allowed to exceed 108° , for above that temperature SbCl_3 comes over in appreciable amounts. It should be noted that the arsenic is reduced to the trivalent state by the Cu_2Cl_2 .

4. *Precipitation of $\text{MgNH}_4\text{AsO}_4$.*—One of the earlier quantitative procedures involves the precipitation of the AsO_4^{---} ion by magnesia mixture in the presence of dilute NH_4OH . Tartrates or oxalates are added to form soluble complexes with SbO_4^{---} ions and prevent its precipitation.

In this procedure, the sulfides are dissolved in aqua regia, HClO_4 , or other strong acidic oxidizing agent. It should be remembered that arsenic cannot be oxidized past the trivalent stage in the presence of a substance more easily oxidizable than H_3AsO_3 . For example, arsenic sulfides cannot be oxidized to H_3AsO_4 in the presence of sulfur. The sulfur is oxidized to SO_2 , which reduces H_3AsO_4 to H_3AsO_3 : $\text{H}_3\text{AsO}_4 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{AsO}_3 + 2\text{H}^+ + \text{SO}_4^{--}$. Time may be saved in making this oxidation by skimming off any globules of molten sulfur by means of a spatula.

Arsenites give no precipitate with magnesia mixture. Error at this point may be avoided by adding a little H_2O_2 to the ammoniacal solution and warming. This will quantitatively oxidize AsO_3^{--} to AsO_4^{---} and ensures precipitation of $\text{MgNH}_4\text{AsO}_4$.

Separation of Antimony.—The following procedures for the separation of antimony are in use:

1. *Precipitation of the Sulfide.*—Antimony sulfides are soluble in hot concentrated HCl but may be precipitated by H_2S from hot 3 *M* HCl solution. A finely divided suspension of Sb_2S_3 is yellow—just the color of As_2S_3 . Upon coagulation (*e.g.*, by boiling), it becomes orange.

2. *Complex Antimony Tartrate and Antimony Oxalate Ions.*—Organic anions, such as $\text{C}_6\text{H}_4\text{O}_6^{--}$ and $\text{C}_2\text{O}_4^{--}$, form complexes with SbO_4^{---} and Sb^{+++} , stable enough to prevent the precipitation of the more soluble antimony compounds—*e.g.*, H_3SbO_4 and many of its salts, H_3SbO_3 and its salts, and the basic antimony salts. The presence of these organic complexing agents does not prevent, but it does hinder, the precipitation of Sb_2S_3 ; *i.e.*, the sulfide forms slowly, and sometimes boiling is necessary to coagulate the precipitate.

Separation of Tin.—Tin is separated by precipitating the other members of the subgroup.

1. *Precipitation of SnS_2 .*—As would be expected from its relatively high solubility (2×10^{-5} mole per liter), SnS_2 cannot be precipitated from HCl solutions of high concentrations (cf. $\text{As}_2\text{S}_{3-5}$, $\text{Sb}_2\text{S}_{3-5}$). Furthermore, tin exists in HCl solution mainly as the chlorostannate ion SnCl_6^{--} , which gives a very low concentration of Sn^{++++} ions. The presence of complexing ions— $\text{C}_2\text{O}_4^{--}$, for example—also prevents its formation.

2. *Reduction of Sn^{++++} .*—The stannic ion is reduced by a number of metals. Active metals, such as zinc and aluminum, reduce it to the metallic state, which must be brought back to the Sn^{++} form by redissolving in HCl. Metals like lead, tin, antimony, and copper reduce it more slowly, and only to the Sn^{++} stage. This eliminates the extra step of redissolving in HCl. The presence of complexing agents retards the reduction, and more time must be allowed for its completion.

When lead is used with solutions containing Cl^- ions, the solution should be thoroughly cooled and any precipitate of PbCl_2 filtered off before the HgCl_2 is added.

The use of ordinary forms of iron, such as nails and iron filings, is not recommended. The ferrous solution obtained from impure iron contains a reducing agent that gives a white precipitate with HgCl_2 solution, spoiling the test for Sn^{++++} . It has been suggested that this reducing action is due to hydrocarbons formed by the carbon present in the iron. FeCl_2 solutions from pure iron do not reduce HgCl_2 solution.

Separation of Mercury.—When Na_2S_x is used to separate the Copper and Tin subgroups, HgS passes into the Tin subgroup. Upon digesting the subgroup sulfides with concentrated HCl, the HgS remains in the residue, along with As_2S_5 and S. After extracting the As_2S_5 by NH_4OH or $(\text{NH}_4)_2\text{CO}_3$, HgS is extracted by aqua regia, and the solution is tested for Hg^{++} with SnCl_2 in the usual way.

Copper in the Tin Subgroup.—When $\text{NH}_4\text{OH} + \text{H}_2\text{S}$ is used instead of $(\text{NH}_4)_2\text{S}_x$ to separate the Copper and Tin subgroups, copper is sometimes carried into the Tin subgroup in the form of a brown CuS_x sol. Since CuS is soluble in concentrated HCl, the Cu^{++} goes into the HCl extract along with Sb^{+++} and Sn^{++++} . It may be detected by adding a drop of $\text{K}_4\text{Fe}(\text{CN})_6$ to a portion of the HCl solution.

Exercises

1. What advantages has the pressure system over the bubbling system for precipitations by H_2S ?

2. Which determines the order in which Group II sulfides are precipitated, their insolubility or the concentration of S^{--} ions in their saturated solutions?

3. Give the formulas and colors of the Group II sulfides. Why is it important to know these colors?

4. Why do sulfides precipitate better in hot rather than in cold solutions? Does heat make them more insoluble?

5. What cations of Group II form complex NH_3 ions? Give their formulas.

6. Explain in terms of ionic equilibrium why Group II is precipitated in the presence of HCl .

7. What would happen if a suspension of CdS was shaken with $\text{Hg}(\text{NO}_3)_2$ solution? Explain the reaction by interlocking equilibriums.

8. What reagents are used to separate the Copper and Tin subgroups? Does it matter which one is used?

9. In general, which type of reaction proceeds faster, a solution with solution or a solution with solid? Would you expect the extraction of the Tin group with $(\text{NH}_4)_2\text{S}_x$ to be rapid?

10. Calculate the concentration of HNO_3 used in separating HgS from the other sulfides of the Copper subgroup.

11. Formulate the equilibriums involved when a suspension of BiOCl is changed to Bi_2S_3 by saturating with H_2S .

12. In a Group II analysis, the dark residue left after boiling the Copper subgroup sulfides with dilute HNO_3 was practically unaffected by aqua regia, and the solution gave no test for Hg^{++} . Suggest what the residue may have contained.

13. What chlorides of Group II may be volatilized and lost by boiling?

14. How could you get a test for Hg^{++} on a solution of HgCl_2 in the presence of an excess of aqua regia?

15. Sometimes Pb^{++} is detected in Group II, but not in Group I. Suggest an explanation. Is Pb^{++} ever found in Group I without also being present in Group II?

16. What step might be omitted in the Group II procedure if Pb^{++} were known to be absent? Is the failure to detect Pb^{++} in Group I sufficient justification for this "short cut"?

17. Why is PbSO_4 readily soluble in $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ but only slightly soluble in $\text{HC}_2\text{H}_3\text{O}_2$?

18. Explain by equilibriums the reaction when a solution of $\text{Pb}(\text{HSO}_4)_2$ is diluted.

19. How would you distinguish between PbCrO_4 and $(\text{BiO})_2\text{Cr}_2\text{O}_7$? Between PbSO_4 and $(\text{BiO})_2\text{SO}_4$?

20. Explain how you can test for Cu^{++} in the presence of Cd^{++} by means of $\text{K}_4\text{Fe}(\text{CN})_6$. What would happen if $\text{Cd}_2\text{Fe}(\text{CN})_6$ were shaken with a Cu^{++} solution?

21. Suppose that CuS were not completely separated from HgS by the dilute HNO_3 treatment. What would happen when the SnCl_2 test was made?

22. Suppose an excess of aluminum were used to separate Cu^{++} and Cd^{++} . What would be the products?

23. Why is $\text{Sn}(\text{OH})_4$ soluble in excess NaOH but not in excess NH_4OH ?
24. Which may be assumed to be more insoluble, orthostannic or metastannic hydroxide?
25. Why will oxalates dissolve $\text{Sb}(\text{OH})_3$ and not Sb_2S_3 ?
26. What sulfide of the Tin subgroup is insoluble in colorless $(\text{NH}_4)_2\text{S}$?
27. What happens when a mixture of $\text{MgNH}_4\text{AsO}_4$ and MgCl_2 is treated with a few drops of AgNO_3 solution? Explain your answer.
28. Explain the action of the NH_4I added in the precipitation of Group II.
29. Why does H_2S precipitate CdS from $\text{Cd}(\text{CN})_4^{--}$ and not Cu_2S from $\text{Cu}(\text{CN})_2^-$?
30. Why do unknowns containing Hg_2^{++} usually give a test for Hg^{++} in Group II?
31. An unknown containing no Bi^{+++} gave a black precipitate in the Na_2SnO_2 test. Suggest a Group II cation that might be responsible for this reaction. Suggest the probable error in technique.
32. What errors might result if the H_2SO_4 solution containing Pb^{++} , Bi^{+++} , Cu^{++} , and Cd^{++} were not "fumed down"?
33. Identify the following ions of Group II:
- A Copper subgroup hydroxide, soluble in excess NH_4OH to a colorless solution.
 - A Tin subgroup anion, giving a brown Ag^+ salt.
 - A colorless cation, forming a yellow oxide with NaOH .
34. Why cannot AsO_3^{---} be oxidized to AsO_4^{---} in the presence of free sulfur?
35. Write the equation for the hydrolysis of $\text{MgNH}_4\text{AsO}_4$ into MgHAsO_4 . How can this hydrolysis be repressed?
36. Write the equation for the hydrolysis of AsCl_5 . Explain the effect of an excess of concentrated HCl in the precipitation of As_2S_5 from AsO_4^{---} solution.
37. Show by equations how you would convert SnS into SnS_2 .
38. Identify the following sulfides of Group II:
- A brown sulfide, soluble in $(\text{NH}_4)_2\text{S}_x$.
 - A yellow sulfide, insoluble in $(\text{NH}_4)_2\text{S}_x$.
 - A brown sulfide, insoluble in $(\text{NH}_4)_2\text{S}_x$.
 - A yellow sulfide, insoluble in concentrated HCl , but soluble in HNO_3 .
 - A black sulfide, insoluble in 2 M HNO_3 .
39. Give reagents and products in the following one-step separations:
- | | |
|---|--|
| (a) CdS and HgS . | (e) Sb_2S_3 and PbS . |
| (b) $(\text{BiO})_2\text{SO}_4$ and PbSO_4 . | (f) Sb^{+++} and Sn^{++++} . |
| (c) As_2S_5 and SnS_2 . | (g) PbS and CdS . |
| (d) Cu^{++} and Bi^{+++} . | (h) Sb^{+++} and Cu^{++} . |
40. How many moles of H_2S would be required completely to precipitate 3 cc. of 2 M $\text{Pb}(\text{NO}_3)_2$, 5 cc. of 5 M $\text{Cu}(\text{NO}_3)_2$, and 2 cc. of 2 M $\text{Bi}(\text{NO}_3)_3$ as sulfides?
41. How many cubic centimeters of 0.3 M $\text{K}_2\text{Cr}_2\text{O}_7$ are required to react completely with 7 cc. of 0.15 M $\text{Pb}(\text{NO}_3)_2$?

42. How many cubic centimeters of 6 *M* NaOH are required to react completely with a solution containing 5 cc. of 0.3 *M* SnCl₂ and 5 cc. of *M* H₂SO₄?

43. What volume of 0.025 *M* H₂S is required to precipitate the sulfides from a solution containing 5 cc. of 0.05 *M* Bi(NO₃)₃ and 5 cc. of 0.05 Cu(NO₃)₂?

44. What volume of 2 *M* HNO₃ would be required to dissolve 0.7710 g. of Bi₂S₃ and 0.8670 g. of CdS (mol. wts.: Bi₂S₃, 514; CdS, 144.5)?

45. What volume of 5 *M* NH₄OH will be required to react completely with a solution containing 2 cc. of 0.2 *M* BiCl₃, 1 cc. of 0.3 *M* CuCl₂, and 4 cc. of 0.4 *M* HCl?

46. What volume of 0.5 *M* SnCl₂ would be required to convert 5 cc. of 0.2 *M* HgCl₂ into Hg₂Cl₂?

47. Suppose that 0.54 g. of Al (at. wt., 27) is added to a mixture of 0.03 mole of SnCl₄ and 0.02 mole of SbCl₃. What would be the composition of the product?

48. What would be the composition of the final mixture if 1.12 g. of iron (at. wt., 56) is added to a solution containing 0.01 mole of CuSO₄, 0.005 mole of CdSO₄, and 0.02 mole of H₂SO₄?

49. How much 0.3 *M* AgNO₃ will be required to react with 0.578 g. of MgNH₄AsO₄·6H₂O?

50. What volume of 3 per cent H₂O₂ would be required to oxidize 0.01 mole of As₂S₃ to AsO₄⁻⁻⁻ + SO₄⁻⁻⁻ in NH₄OH solution?

51. What weight of Na₂SO₃ (mol. wt., 126) will be required to convert 10 cc. of 0.5 *M* H₃AsO₄ into H₃AsO₃? How many moles of H₂SO₄ will be formed?

52. What volume of *M* NaCN will be required to react with an NH₄OH solution containing 0.002 mole of Cu(NH₃)₄SO₄ and 0.003 mole of Cd(NH₃)₄SO₄?

53. Devise a procedure for separating Ag⁺, Hg⁺⁺, and Cd⁺⁺, all other metallic ions being absent. Omit all unnecessary steps.

54. An unknown was in the form of a clear solution. After the acidity had been regulated to 0.24 *M* H⁺, the solution was saturated with H₂S, giving a brownish precipitate. This precipitate was warmed with (NH₄)₂S_x, giving a black residue (1) in a yellow solution (2). The black residue (1) was dissolved in hot dilute HNO₃, and the solution was evaporated to SO₃ fumes with H₂SO₄, cooled, and diluted. A white precipitate (3) formed, soluble in NH₄C₂H₃O₂ to a solution that gave with K₂Cr₂O₇ a yellow precipitate insoluble in HC₂H₃O₂. The filtrate from precipitate (3) was treated with NH₄OH, giving a white precipitate (4), which turned brown on the filter when the H₂S in the laboratory came into contact with it. The filtrate from (4) was practically colorless, though a portion of it gave a rose color with H₂SO₄ + K₄Fe(CN)₆. The remainder of the filtrate from (4) was treated with NaCN + H₂S without effect.

Yellow solution (2) was acidified with HCl, giving a yellow precipitate (5). Precipitate (5) was extracted with hot concentrated HCl, giving a colorless solution (6) and a yellow residue (7). Residue (7) was heated with HNO₃,

filtered from the sulfur residue, and neutralized with NH_4OH . Upon addition of AgNO_3 , a chocolate-brown precipitate formed. Solution (6) was diluted and saturated with H_2S , giving an orange precipitate. What ions were indicated?

55. Upon regulating the acidity upon an unknown containing Group II cations only, a white turbidity appeared. Without filtering, the solution was saturated with H_2S , forming a brownish precipitate. After filtering, the precipitate was treated with warm $(\text{NH}_4)_2\text{S}_x$, leaving a brown residue (1) and a yellow solution (2). Residue (1) was partially soluble in boiling 2 *M* HNO_3 , leaving a heavy black residue and a colorless solution. The solution was evaporated to SO_3 fumes with H_2SO_4 and on dilution gave no precipitate. Excess NH_4OH was added, and a white precipitate formed. The filtrate from this precipitate gave a yellow precipitate with H_2S .

The solution (2) was acidified with HCl , giving a yellow precipitate (3). Precipitate (3) was dissolved in hot concentrated HClO_4 , $\text{H}_2\text{C}_2\text{O}_4$ was added, and the solution was treated with H_2S + a drop of NH_4I solution, forming a yellow precipitate (4) and a filtrate (5). Precipitate (4) was insoluble in hot concentrated HCl , but redissolved in HClO_4 , forming a solution that gave a white precipitate with $\text{Mg}(\text{NO}_3)_2 + \text{NH}_4\text{OH}$. Filtrate (5) was boiled with lead foil, with no visible effect. However, after cooling and filtering, HgCl_2 was added, giving a gray-black precipitate.

What ions were indicated?

56. A colorless solution, containing Group II cations only, was saturated with H_2S , giving at first a white precipitate, which progressively changed to yellow, then orange, and finally black. This H_2S precipitate was warmed with $(\text{NH}_4)_2\text{S}_x$, leaving a black residue (1) and a filtrate (2). The residue (1) dissolved only partially in hot 2 *M* HNO_3 , leaving a black residue. The filtrate was evaporated with H_2SO_4 to SO_3 fumes, and, upon dilution, a slight white precipitate (3) formed. This precipitate was boiled with NaOH , and the filtrate was acidified with $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{K}_2\text{Cr}_2\text{O}_7$ added without effect. The filtrate from precipitate (3) gave with NH_4OH a voluminous white precipitate (4). The filtrate from precipitate (4) was acidified with H_2SO_4 , and a few drops of $\text{K}_4\text{Fe}(\text{CN})_6$ were added, giving a yellowish white precipitate.

Filtrate (2) was acidified with HCl , giving a white precipitate insoluble in concentrated HCl and insoluble in NH_4OH .

What ions were indicated?

CHAPTER XVI

GROUP III—THE AMMONIUM SULFIDE GROUP

Group III, as described in this chapter, was formerly divided into two major groups, known as the *ammonium hydroxide group* and the *ammonium sulfide group*. A number of textbooks on qualitative analysis still follow this earlier grouping. The membership and analysis of these older groups are outlined under the Ammonium Hydroxide and Ammonia Complex subgroups (pages 269-275).

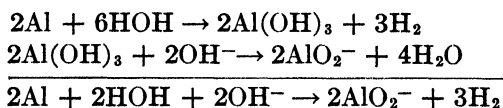
Membership.—Group III, as herein given, contains the cations whose sulfides are not precipitated by H_2S in dilute acid solution but whose sulfides or hydroxides are precipitated by $(\text{NH}_4)_2\text{S}$ (*i.e.*, $\text{NH}_4\text{OH} + \text{H}_2\text{S}$). It is variously divided into subgroups, depending upon the procedure used. In the following list, rarer ions, not included in ordinary procedures, are designated by brackets.

Aluminum, Al^{+++}	Manganous, Mn^{++}
Chromium, Cr^{+++}	Ferrous, Fe^{++}
Zinc, Zn^{++}	Ferric, Fe^{+++}
[Uranium, UO_2^{++}]	Cobalt, Co^{++}
[Vanadium, $\text{V}_2\text{O}_2^{++++}$]	Nickel, Ni^{++}
[Beryllium, Be^{++}]	

ALUMINUM

The Metal.—Aluminum is a soft, white metal, used extensively in cooking utensils, “silver” paint, and light alloys. It dissolves slowly in cold HCl but rapidly upon heating. Dilute H_2SO_4 scarcely dissolves it at all, but concentrated H_2SO_4 dissolves it rapidly with the evolution of SO_2 . It is insoluble in HNO_3 , probably owing to the formation of a layer of insoluble Al_2O_3 , which exerts a protective action on the metal. Aluminum dissolves in hot KOH and NaOH solutions with the evolution of hydrogen. This action is not due to any acidic property of these hydroxides. The hydrogen comes from the water and not from

the alkali. The function of the latter is to keep the surface of the metal clean by removing the Al(OH)_3 as fast as it is formed.



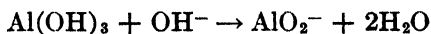
The Ions.—Aluminum forms the trivalent cation Al^{+++} and the univalent anion AlO_2^- .

Solubility of Compounds.—Most of the salts of aluminum are soluble, though with a certain amount of hydrolysis; *e.g.*, aluminum chloride, AlCl_3 , aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$, etc. The most important of the insoluble compounds is the hydroxide, Al(OH)_3 . The phosphate, AlPO_4 , and the basic acetate, $\text{Al(OH)}_2\text{C}_2\text{H}_3\text{O}_2$, are also met as precipitates in analytical work.

Aluminum Hydroxide.— Al(OH)_3 is formed as a white gelatinous precipitate by the reaction of Al^{+++} ions with alkaline solutions, such as NaOH , NH_4OH and Na_2CO_3 . It is very insoluble—only 3.7×10^{-15} mole per liter, according to one authority. As would be expected in highly insoluble substances (see page 29), the precipitate is colloidal. Really, part of it remains in solution as a sol, and precipitation is complete only when the solution is heated and when it contains an electrolyte.

Aluminum hydroxide is soluble enough in water to give sufficient OH^- ions to react with acids and sufficient H^+ ions to react with strong bases. That is, it is amphoteric (see page 111). It is slightly soluble in weak acids and weak bases. Unless its basicity is reduced by the presence of NH_4^+ ions, NH_4OH will dissolve appreciable amounts.

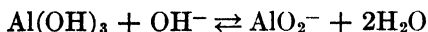
The solution of Al(OH)_3 in NaOH solution contains aluminum in the form of an aluminate ion. A timely question is, Which aluminate is it, the orthoaluminate, AlO_3^- , or the metaaluminate, AlO_2^- ? This has been answered by titrating a precipitate of Al(OH)_3 by NaOH solution. It was found that 1 mole (really, slightly more) of the base was required to dissolve 1 mole of Al(OH)_3 . Therefore the equation must be



If the orthoaluminate was formed, 3 gram ions of OH^- would be required.

Such a result is to be expected. In all polybasic acids, the first H atom is much more active than the second, and the second more active than the third, etc. Since aluminic acid, H_3AlO_3 , is a very weak acid, the tendency of the second and third H atoms to ionize is negligible.

The relation between the solubility of $\text{Al}(\text{OH})_3$ in alkaline solutions and the OH^- -ion concentration may be deduced by means of the mass law. In the equilibrium



$\text{Al}(\text{OH})_3$ is present as a saturated solution, and H_2O is present in large excess, so that their concentrations may be assumed to be constants. Therefore the equilibrium constant may be written thus:

$$K_{\text{equilibrium}} = \frac{[\text{AlO}_2^-][\text{H}_2\text{O}]^2}{[\text{Al}(\text{OH})_3][\text{OH}^-]} = \frac{[\text{AlO}_2^-] \times k_1}{k_2 \times [\text{OH}^-]} = k_3 \frac{[\text{AlO}_2^-]}{[\text{OH}^-]}$$

Since the dissolved $\text{Al}(\text{OH})_3$ is almost wholly in the form of AlO_2^- ions, the concentration of AlO_2^- ions may be taken as a measure of the solubility of the $\text{Al}(\text{OH})_3$. According to the above expression, the ratio between the concentrations of AlO_2^- and OH^- ions is a constant, the solubility of $\text{Al}(\text{OH})_3$ varying directly as the alkalinity of the solution. That is, as long as there are any OH^- ions present, there must be a proportional amount of AlO_2^- .

Calculation of the Solubility of $\text{Al}(\text{OH})_3$ in NH_4OH .—Assuming that the solubility product of aluminic acid is $[\text{H}^+][\text{AlO}_2^-] = 10^{-14}$, the solubility in M NH_4OH (0.4 per cent ionized) may be calculated as follows:

Substituting the OH^- -concentration of M NH_4OH in the expression for the ion product of water

$$[\text{H}^+][\text{OH}^-] = [\text{H}^+] \times 0.004 = 1 \times 10^{-14}$$

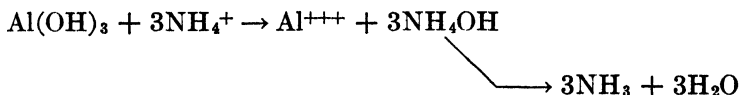
$[\text{H}^+]$ is found to be 250×10^{-14} , or 2.5×10^{-12} . Substituting this value in the solubility product for aluminic acid

$$2.5 \times 10^{-12} \times [\text{AlO}_2^-] = 1 \times 10^{-14}$$

$$[\text{AlO}_2^-] = 0.4 \times 10^{-2}, \text{ or } 0.004 M$$

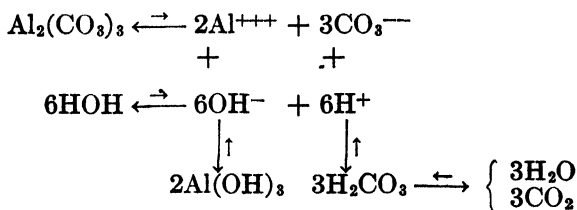
That is, the solubility of $\text{Al}(\text{OH})_3$ in M NH_4OH is 78×0.004 , or 0.312 g. per liter.

Consequently an excess of OH^- must be avoided if $\text{Al}(\text{OH})_3$ is to be completely precipitated. This is realized by adding a slight excess of NH_4OH to the boiling solution of the Al^{+++} , containing NH_4^+ , and then depending upon the heat to volatilize the excess. Continued boiling will result in partial re-solution of the precipitate by the NH_4^+ ion present.



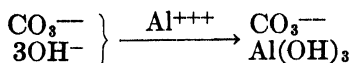
Upon ignition, $\text{Al}(\text{OH})_3$ is converted into Al_2O_3 , which is insoluble in acids, probably owing to its failure to add water and re-form $\text{Al}(\text{OH})_3$.

Hydrolysis of Salts.—Owing to the weakness of $\text{Al}(\text{OH})_3$ as a base, there is a strong tendency for Al^{+++} ions to combine with the OH^- ions from the water to form $\text{Al}(\text{OH})_3$, which is not only very slightly ionized but also very insoluble. This disposition to hydrolysis will be further favored if the anion of the Al^{+++} salt tends to unite with H^+ ions to form a weak or insoluble acid. This is exactly the situation with the carbonate, $\text{Al}_2(\text{CO}_3)_3$, and the sulfide, Al_2S_3 . The tendency of Al^{+++} to form $\text{Al}(\text{OH})_3$ and of CO_3^{--} and S^{--} to form the weak acids H_2CO_3 and H_2S is so strong that the forward reaction runs to completion in these cases. For example

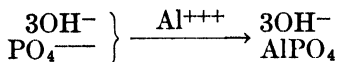


The hydrolysis of Al_2S_3 may be formulated similarly.

This should not be taken to imply that when an Al^{+++} solution is treated with Na_2CO_3 solution, $\text{Al}_2(\text{CO}_3)_3$ is first formed and subsequently hydrolyzes. Na_2CO_3 solution is largely hydrolyzed and contains a considerable concentration of OH^- ions. Upon mixing with the Al^{+++} solution, the Al^{+++} ion has its choice between the CO_3^{--} and the OH^- ions and combines with the latter since $\text{Al}(\text{OH})_3$ is more insoluble than $\text{Al}_2(\text{CO}_3)_3$.



A different situation arises in the case of AlPO_4 . The PO_4^{--} ion tends to combine with H^+ ions from the water, forming the weakly acidic ion HPO_4^{--} —exactly analogous to the preceding case. But this tendency is offset by the insolubility of AlPO_4 , which seems to furnish an even lower concentration of Al^{+++} ions than $\text{Al}(\text{OH})_3$.



AlPO_4 , then, does not conform to the dubious rule that "salts of very weak bases and very weak acids are completely hydrolyzed."

In hot neutral solutions, Al^{+++} combines with the $\text{C}_2\text{H}_3\text{O}_2^-$ ion to form insoluble basic aluminum acetate, to which has been assigned the approximate formula $\text{Al}(\text{OH})_2\text{C}_2\text{H}_3\text{O}_2$. This is a case of partial hydrolysis. The course of the reaction is determined by several influences: (1) the low solubility of the basic acetate, (2) the removal of H^+ ions by $\text{C}_2\text{H}_3\text{O}_2^-$ as molecular $\text{HC}_2\text{H}_3\text{O}_2$, and (3) the increase in ionization of water by heat.

Organic Complexes.—Aluminum hydroxide is soluble in a number of organic compounds—principally those containing hydroxyl (OH) groups. Glycerin, the sugars, starch, tartrates, etc., are representative. The chemical nature of the products is not definitely known. In the presence of such substances, Al^{+++} is not thrown down at all in Group III but passes into subsequent groups. This interference is met by oxidizing these materials by HNO_3 in regulating the acidity before the precipitation of Group II. This solvent action, on the other hand, gives a method for separating Al^{+++} from certain other cations; *e.g.*, $(\text{NH}_4)_2\text{S}$ precipitates Fe_2S_3 from an Al^{+++} - Fe^{+++} solution containing tartrates.

Lake Formation.— $\text{Al}(\text{OH})_3$ is a positive colloid (see page 26); *i.e.*, it carries a positive electric charge. Most dyes, on the other hand, are negatively charged. When a salt of a dye is mixed with an Al^{+++} solution and the mixture is made slightly alkaline, the $\text{Al}(\text{OH})_3$ and dye combine to form an insoluble "lake," with a color that is frequently distinctive. The NH_4 salt of aurintrin-

carboxylic acid, $C_{22}H_{14}O_9$, sold under the trade name of *aluminon*, gives with $Al(OH)_3$ a bright red lake. $Fe(OH)_3$, also a positive colloid, forms a reddish-brown lake. $Si(OH)_4$, on the other hand, is a negative colloid and does not combine with negative dyes like aluminon. Hence the dye is not absorbed.

Thenard's Blue.— Al_2O_3 has acid properties and combines with certain oxides at high temperatures, forming aluminates. For example, if a mixture of $Co(NO_3)_2$ and $Al(NO_3)_3$ is fused, the oxides first formed unite to give blue cobalt aluminate, $Co(AlO_2)_2$.



This is the basis of the Thenard blue reaction, formerly used as a confirmatory test for Al. There are a number of interferences; and an excess of $Co(NO_3)_2$ forms black CoO , which masks the blue color of the $Co(AlO_2)_2$.

CHROMIUM

The Metal.—Metallic chromium is a very hard, brittle metal, with a silver-like luster. It is soluble in HCl and dilute H_2SO_4 , forming the chromous ion Cr^{++} . It is insoluble in HNO_3 . It is used in plating metals to give a noncorrodible surface and in making chrome steels. It will be remembered that chrome steels are very hard and, for a certain range of chromium, "stainless" or slow corroding.

The Ions.—Chromium forms three distinct series of compounds, showing the valences two, three, and six. In the first and second of these series, the element is metallic, forming cations; and in the third, acidic, forming anions.

Cations	Anions
[Chromous, Cr^{++}]	Chromite (meta), CrO_2^-
Chromic, Cr^{+++}	Chromate, CrO_4^{--}
	Dichromate, $Cr_2O_7^{--}$

The chromous ion is a very active reducing agent, being oxidized by the air to Cr^{+++} . The use of brackets in its case indicates that it is never met in ordinary qualitative analyses.

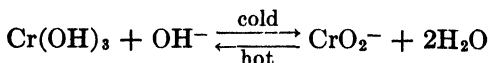
In addition to CrO_4^{--} and $Cr_2O_7^{--}$, hexavalent chromium probably forms the hydrogen chromate anion $HCrO_4^-$. No solid hydrogen chromates have been isolated, but certain reactions indicate that they probably exist in solution.

The perchromate anion, formed by reaction with peroxides, has been studied, but its constitution is probably not fully understood.

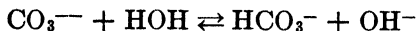
Chromic Compounds

Soluble Chromic Salts.—The Cr^{+++} ion forms soluble salts with Cl^- , NO_3^- , SO_4^{--} , etc. The usual color of their solutions is green, though the Cr^{+++} ion itself may be violet. These salts are used in tanning leather, making paint stuffs, and as mordants in the textile industry.

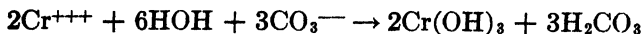
Chromic Hydroxide.—The most important of the insoluble chromic compounds is the hydroxide, $\text{Cr}(\text{OH})_3$. It is formed as a grayish-green, gelatinous precipitate when a basic solution is added to a solution of Cr^{+++} ions—*e.g.*, NH_4OH , dilute NaOH or KOH , Na_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$, etc. It is soluble in excess of cold NaOH or KOH , forming a clear green solution containing the chromite ion CrO_2^- . Upon boiling, $\text{Cr}(\text{OH})_3$ is reprecipitated. These reactions may be represented thus:



The precipitation of $\text{Cr}(\text{OH})_3$ by alkaline carbonates is due to the CO_3^{--} being considerably hydrolyzed by water.



Of the three anions available, Cr^{+++} preferentially combines with OH^- , indicating that $\text{Cr}(\text{OH})_3$ is the most insoluble possibility. The over-all reaction may be written:



For similar reasons, $(\text{NH}_4)_2\text{S}$ also precipitates $\text{Cr}(\text{OH})_3$.

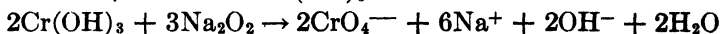
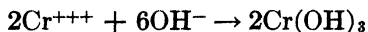


Upon ignition, $\text{Cr}(\text{OH})_3$ forms Cr_2O_3 .

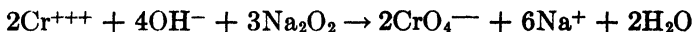
Ammonia Complex.—Sometimes the filtrate from a precipitation of $\text{Cr}(\text{OH})_3$ by NH_4OH is lavender in color. This is due to a chromic ammonia complex, probably $\text{Cr}(\text{NH}_3)_6^{+++}$. The formation of this complex is favored by large amounts of NH_4^+ ions. The complex is decomposed by boiling, precipitating $\text{Cr}(\text{OH})_3$. Evidently its formation may be avoided by precipitating the $\text{Cr}(\text{OH})_3$ from boiling solutions.

Chromic Acetates.—Pure Cr^{+++} solutions may be treated with alkaline acetates at the boiling point without the formation of an insoluble basic acetate [*cf.* $\text{Al}(\text{OH})_2\text{C}_2\text{H}_3\text{O}_2$]. However, if considerable amounts of Al^{+++} or Fe^{+++} are present, the Cr^{+++} is wholly precipitated as $\text{Cr}(\text{OH})_2\text{C}_2\text{H}_3\text{O}_2$. If Cr^{+++} is present in excess, the precipitation, not only of Cr^{+++} , but also of Al^{+++} and Fe^{+++} , is incomplete. Evidently the basic acetate precipitation is not dependable in the presence of Cr^{+++} ions.

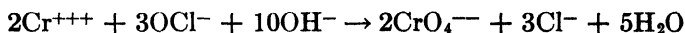
Oxidation to Chromate by Peroxides.—Sodium peroxide, Na_2O_2 , or H_2O_2 in alkaline medium, converts Cr^{+++} into yellow CrO_4^{--} . $\text{Cr}(\text{OH})_3$ may be regarded as an intermediate product.



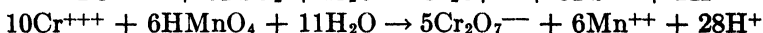
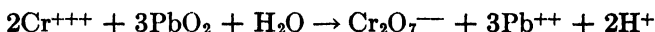
Adding,



Other strong oxidizing agents behave similarly.

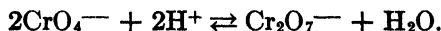


Since chromates in acid solution are strong oxidizing agents, still stronger oxidizing agents are required to form them from Cr^{+++} . For example, PbO_2 in the presence of HNO_3 , or HMnO_4 ,



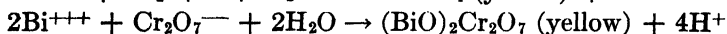
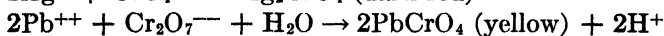
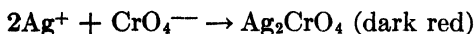
Chromates and Dichromates

The Chromate-dichromate Equilibrium.—Acids convert soluble chromates into dichromates, and bases convert soluble dichromates into chromates. The equilibrium may be expressed:

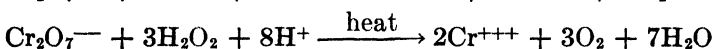
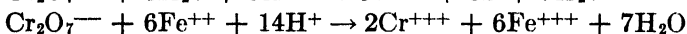
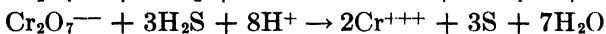
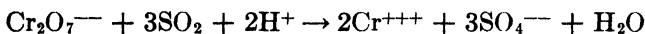


It is believed that this simple relation does not show all the ions involved. Probably HCrO_4^- ions are formed as an intermediate product (see page 195).

CrO_4^{--} and $\text{Cr}_2\text{O}_7^{--}$ ions react with most of the cations forming chromates (less frequently dichromates), insoluble in water, but soluble in strong acids; *e.g.*,



Oxidizing Action.—Chromates in acid solution and dichromates are good oxidizing agents, reacting with reducing agents, forming Cr^{+++} ions. The following equations are representative:



If the solution is neutral or alkaline, the reaction will be incomplete. For example, when a $\text{K}_2\text{Cr}_2\text{O}_7$ solution is saturated with H_2S , the mixture slowly turns brown, owing to the reduction of part of the $\text{Cr}_2\text{O}_7^{--}$ to Cr^{+++} , which then combines with CrO_4^{--} forming brown chromic chromate, $\text{Cr}_2(\text{CrO}_4)_3$.

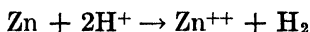
The Chromate Peroxide Reaction.—A very interesting reaction is the formation of a blue liquid when H_2O_2 is added to an acidified solution of a chromate or dichromate. This liquid is stable for a short time in cold water but is instantly decomposed upon heating. For this reason, it is extracted by an organic reagent immediately after its formation. Ethyl ether, $(\text{C}_2\text{H}_5)_2\text{O}$, is usually employed. This blue liquid has been called *perchromic acid*, and such formulas as H_3CrO_7 and H_3CrO_8 have been assigned to it. It must be said that it does not have the properties of a true peracid, and it is doubtful if its real nature is yet known.

Detection.—Owing to the strong colors of its ions, chromium has an insistent way of showing its presence throughout a qualitative analysis. A green color in the original solution, unchanged by treatment with H_2S , and a gray-green hydroxide in Group III, converted into a yellow solution by Na_2O_2 , are a sufficient test for Cr^{+++} ions. If the original solution was yellow or orange in color and became green upon treatment with H_2S in Group II, CrO_4^{--} or $\text{Cr}_2\text{O}_7^{--}$ ions are indicated. When these color effects are lacking or are masked by other colors in the solution, the H_2O_2 test is applied. It should be remembered that this last reaction is a test for CrO_4^{--} ions; Cr^{+++} ions do not give it.

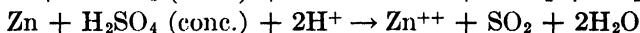
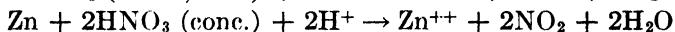
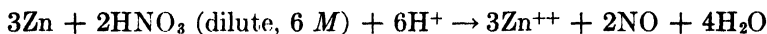
ZINC

The Metal.—Zinc is a bluish-white metal, extensively used industrially, *e.g.*, in galvanized iron, dry cells, alloys of the brass type, etc.

Ordinary zinc (spelter) dissolves in all the common acids. With nonoxidizing acids, such as HCl or dilute H_2SO_4 , hydrogen is evolved.



With oxidizing acids, the usual reduction products of the acids are obtained.



Zinc dissolves in solutions of strong alkalies, NaOH and KOH, liberating H_2 and forming HZnO_2^- anions. Here again (*cf.* Aluminum, page 240), the hydrogen comes from the water: $\text{Zn} + 2\text{HOH} \rightarrow \text{H}_2 + \text{Zn(OH)}_2$. The alkali aids by dissolving the Zn(OH)_2 , which otherwise would stop the reaction.

Zinc Hydroxide.— Zn^{++} ions combine with OH^- ions, forming white, gelatinous Zn(OH)_2 , soluble in acids, bases, and NH_3 solutions.

The solubility of Zn(OH)_2 in both acids and bases has been explained (page 112) by its dual ionization.



Basic ionization

Acidic ionization

Zinc Sulfide.— Zn^{++} ions react with S^{--} ions, forming white ZnS . Zinc sulfide is the most insoluble sulfide of Group III, having a solubility product of 1.2×10^{-23} . It is insoluble in $\text{HC}_2\text{H}_3\text{O}_2$, though readily soluble in strong acids. ZnS is insoluble in $(\text{NH}_4)_2\text{S}$; it appears to have no acid properties.

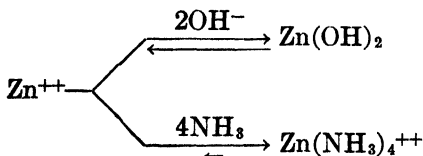
Zinc Ferrocyanide.— Zn^{++} ions react with ferrocyanides (*e.g.*, $\text{K}_4\text{Fe(CN)}_6$), forming as a primary product zinc ferrocyanide,

* The formula for the zincate ion is commonly written ZnO_2^{--} . This is wrong; for zincic acid, H_2ZnO_2 , is a very weak acid, and the ionization of weak acids is limited to their first H atom. So it is to be considered a monobasic acid, like H_2PbO_2 and H_2AlO_2 (see pp. 175, 242).

$\text{Zn}_2\text{Fe}(\text{CN})_6$. This compound adds $\text{K}_4\text{Fe}(\text{CN})_6$, giving as a final product $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$. This precipitate is insoluble in dilute acids but is decomposed by strong bases.

Zinc Ammonia Complex Ions.—The Zn^{++} ion adds NH_3 , forming the complex ion $\text{Zn}(\text{NH}_3)_4^{++}$. This complex ion is moderately stable; its instability constant (see page 118) has the value 2.6×10^{-10} . As a result, only the more soluble zinc compounds, such as $\text{Zn}(\text{OH})_2$ and ZnCO_3 , are soluble in NH_3 solutions; the more insoluble compounds, such as ZnS , are not dissolved.

Again, it must be insisted that $\text{Zn}(\text{OH})_2$ is not an intermediate compound in the formation of $\text{Zn}(\text{NH}_3)_4^{++}$ ions. When NH_4OH is added to a Zn^{++} solution, the concentration of OH^- ions may be large enough at first to exceed the solubility product of $\text{Zn}(\text{OH})_2$, and partial precipitation may take place. Later, the NH_3 concentration reaches the point at which $\text{Zn}(\text{NH}_3)_4^{++}$ becomes the stable product and the $\text{Zn}(\text{OH})_2$ goes back into solution. The situation may be represented thus:



Reducing Action of Metallic Zinc.—In acid medium, zinc is an active reducing agent, reducing ClO_3^- to Cl^- , Fe^{+++} to Fe^{++} , AgCl to Ag , HgS to $\text{Hg} + \text{H}_2\text{S}$, trivalent arsenic to AsH_3 , etc.

The strong reducing action of metallic zinc is related in some way to the difficulty of discharging H^+ ions on zinc. If very pure zinc is placed in dilute H_2SO_4 , there will be no reaction. However, if a piece of copper or platinum is brought into contact with the zinc, the zinc begins to dissolve by sending Zn^{++} ions into solution. The displaced H^+ ions of the acid separate as gaseous H_2 , not on the zinc, but on the copper or platinum. In order to discharge H^+ ions on zinc, an extra potential of about -0.78 volt must be given to the zinc. The excess potential necessary to discharge H^+ ions on a metal is known as *overvoltage*. Other metals show similar effects, but the excess voltage is not so great (see Table 18, page 155). An analogous positive overvoltage is necessary to discharge OH^- ions on certain metals.

The excess energy required to discharge H^+ ions on zinc reappears in increased intensity of the reducing action. Now, the lower the H^+ -concentration, the higher the potential necessary to discharge H^+ ions. It follows then that the potential must be much higher in alkaline solution, where the number of H^+ ions is exceedingly small. This means that the reducing action of zinc in alkaline solution is greater than in acid solution, and such seems to be the case. For example, zinc dust in NaOH solution will reduce NO_3^- to NH_3 . In acid solution, the reduction product is NO, mainly.

The mechanism of these reactions is largely a matter of speculation. According to the theory of nascent action, the reducing agent is not zinc, but hydrogen liberated by the zinc. This hydrogen forms first as molecules of monatomic hydrogen, later changing into diatomic hydrogen: $2H \rightarrow H_2$. The monatomic, or "nascent," form is much more reactive than the ordinary diatomic hydrogen.

There are several considerations that support the theory of nascent action. (1) The zinc does not have to be in actual physical contact with the material to be reduced, but the two may be separated by easily perceptible distances. For example, if a piece of zinc is supported on a plug of glass wool in a test tube and acidified $KMnO_4$ solution is introduced, the part of the solution below the plug is decolorized about as soon as the portion above. Diffusion seems too slow to account for this "reaction at a distance." (2) The reducing agent cannot be H_2 , for this gas may be bubbled through most oxidizing solutions without effect. Both of these phenomena may be explained by assuming that the reducing agent is monatomic hydrogen, more or less soluble in water.

On the other hand, there are certain aspects of the action that are hard to explain by the theory of nascent action. The reducing intensity is not always the same but varies with the metal liberating the hydrogen. For example, the "nascent hydrogen" from aluminum and dilute H_2SO_4 does not reduce $AgCl$, but that from zinc and dilute H_2SO_4 reduces it to metallic silver. We must conclude either that the energy content of nascent hydrogen varies with its source or that the metal is the actual reducing agent after all.

Rinmann's Green.—If a solution of $\text{Zn}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$ is evaporated to dryness and the residue is ignited, the mixture of ZnO and CoO first formed seems to combine, forming a green cobalt zincate, CoZnO_2 , called *Rinmann's green*. The reaction was formerly used as a confirmatory test for Zn , but numerous interferences have reduced its popularity. An excess of black CoO completely masks the green color.

Detection.—After all, the most distinctive reaction of Zn^{++} ions is the formation of white ZnS , insoluble in $\text{HC}_2\text{H}_3\text{O}_2$, but soluble in HCl . Most interferences are results of careless technique. Sometimes a white precipitate of sulfur appears, owing to the presence of H_2O_2 from Na_2O_2 , or of CrO_4^{--} , when these substances have not been completely removed. S and ZnS may be separated by extracting the mixture with HCl and reprecipitating the Zn^{++} in the filtrate as ZnS by means of NH_4OH and H_2S . The formation of a white precipitate with $\text{K}_4\text{Fe}(\text{CN})_6$, insoluble in dilute HCl , has been recommended, but the reaction does not seem to have any advantages over the ZnS test.

MANGANESE

The Metal.—Manganese is a steel-colored metal, very hard and brittle, and readily tarnished by air. It decomposes water, even in the cold, and dissolves in all the common acids (including acetic), forming manganous ions Mn^{++} . Metallic manganese is used in steelmaking.

Ions.—Manganese forms several series of compounds, with valences ranging from +2 to +7. Of these, the only cation met in qualitative analysis is the manganous ion Mn^{++} , and the only anion is the permanganate ion MnO_4^- . The trivalent manganic ion Mn^{+++} and the manganate ion MnO_4^{--} are decomposed by water, with the separation of MnO_2 .



Quadrivalent manganese is represented by a single, but very important, compound—manganese dioxide, MnO_2 .

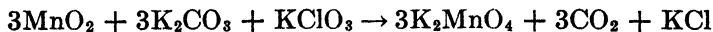
Soluble and Insoluble Compounds.—The insoluble compounds of analytical importance are the sulfide, MnS , and the dioxide, MnO_2 . The Mn^{++} salts of the common anions are soluble—

e.g., MnCl_2 , $\text{Mn}(\text{NO}_3)_2$, MnSO_4 , etc. All permanganates are soluble.

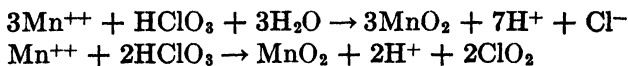
Manganous Hydroxide.— Mn^{++} ions react with the alkalis to form manganous hydroxide, $\text{Mn}(\text{OH})_2$ —white, but readily oxidized by the air, the color changing through tan to brown-black. The final product is usually considered to be hydrated MnO_2 [written $\text{MnO}_2 \cdot \text{H}_2\text{O}$, $\text{MnO}(\text{OH})_2$, or H_2MnO_3], though some authors consider it to be $\text{Mn}(\text{OH})_3$. $\text{Mn}(\text{OH})_2$ is appreciably soluble in water— 2.2×10^{-5} mole per liter. As a result, NH_4OH in the presence of NH_4^+ ions does not give a sufficient concentration of OH^- ions to precipitate $\text{Mn}(\text{OH})_2$ (*cf.* $\text{Mg}(\text{OH})_2$, page 301).

Manganous Sulfide.— Mn^{++} solutions react with $(\text{NH}_4)_2\text{S}$ to form salmon-colored MnS , easily soluble in acids, even in $\text{HC}_2\text{H}_3\text{O}_2$. MnS is the most soluble sulfide met in the entire analytical procedure. Its solubility in water is 3.8×10^{-8} mole per liter, indicating a solubility product of 1.4×10^{-15} .

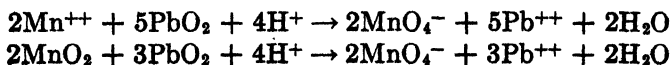
Oxidation of Manganous Compounds.—In alkaline medium, Mn^{++} compounds are slowly oxidized by the air, forming MnO_2 , thus: $2\text{Mn}^{++} + 4\text{OH}^- + \text{O}_2 \rightarrow 2\text{MnO}_2 \cdot \text{H}_2\text{O}$. More active oxidizing agents, such as Na_2O_2 , oxidize them more rapidly. Still stronger oxidizing agents, such as fused KNO_3 or KClO_3 , oxidize Mn^{++} to MnO_4^- .



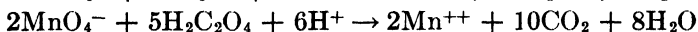
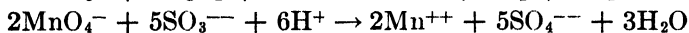
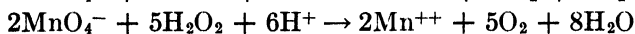
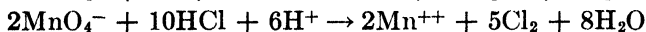
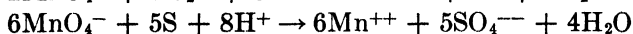
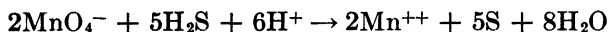
It is harder to oxidize Mn^{++} in acid solution, and the most powerful oxidizing agents are required. Chloric acid (*i.e.*, $\text{KClO}_3 + \text{HNO}_3$) slowly oxidizes Mn^{++} to MnO_2 . The equation is variously written.



Probably both reactions proceed simultaneously. In the first equation, the Cl^- is oxidized to Cl_2 by the excess HNO_3 ; otherwise it would tend to react with MnO_2 , reducing it back to Mn^{++} . Still more vigorous oxidizing agents oxidize Mn^{++} to MnO_4^- —*e.g.*, PbO_2 in the presence of HNO_3 .

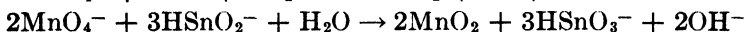
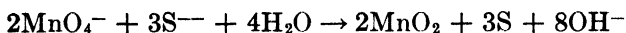


Reduction of Permanganates.—Permanganates in acid solution are very strong oxidizing agents and are readily reduced to Mn^{++} .



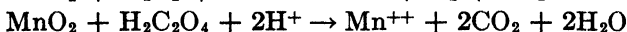
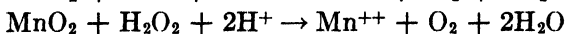
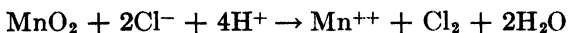
The reactions with H_2S deserve special attention. With an excess of MnO_4^- , the H_2S may be completely oxidized to SO_4^{--} . As the concentration of the MnO_4^- is diminished, the oxidation is less vigorous, and the H_2S is oxidized to the S stage, mainly. The SO_4^{--} formed in this way tends to precipitate Ba^{++} in Group II to a certain extent.

In alkaline solution, the reduction does not run so smoothly. MnO_2 , and not Mn^{++} , is the reduction product.

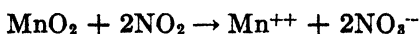


In both acid and alkaline mediums, permanganates react with paper. Hence permanganate solutions cannot be filtered through paper filters. Asbestos or sintered glass must be used.

Manganese Dioxide.—As just stated, this compound is formed by mild oxidation of Mn^{++} in alkaline medium or by strong oxidation in acid medium. This suggests that MnO_2 should be a good oxidizing agent in acid medium, and such is the case.



MnO_2 is soluble in reducing acids or in acids containing a reducing agent. If the reducing agent is absent, there is no reaction. For example, MnO_2 is insoluble in H_2SO_4 , HNO_3 , and HClO_4 . It does dissolve readily in "yellow" HNO_3 , owing to the presence of oxides of nitrogen, which act as reducing agents; *e.g.*,



Manganese dioxide is used industrially in dry cells and glassmaking and as a drier for paints.

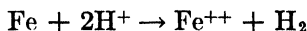
Manganate Formation.—When an Mn compound is fused in an Na_2CO_3 - KClO_3 mixture (see page 253), a green manganate is formed. This reaction was formerly used as a test for Mn^{++} but has been discontinued on account of interferences.

Detection.—The detection of Mn^{++} in a solution is based upon the following reactions: (1) the formation of brown-black MnO_2 upon heating with KClO_3 and concentrated HNO_3 ; (2) the formation of a rose color upon warming Mn^{++} or MnO_2 with PbO_2 in the presence of HNO_3 .

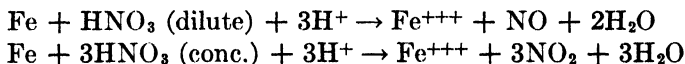
IRON

The Metal.—Metallic iron is too familiar to need description. It is the base of numerous industrial alloys, including cast irons and steel, which sometimes present very interesting problems for the analyst.

Iron dissolves readily in dilute acids. With HCl or H_2SO_4 , which have no oxidizing action, the products are the ferrous ion and hydrogen.



With ordinary dilute HNO_3 , ferric ions and nitric oxide are the products; and with hot concentrated HNO_3 , ferric ions and nitrogen dioxide.



Cold concentrated HNO_3 has no apparent effect on iron. Probably the iron is coated with a protective film of Fe_3O_4 , which is insoluble in HNO_3 . Iron in this form is said to be passive.

Series of Compounds.—Iron forms two series of compounds: (1) ferrous, in which the element is bivalent, and (2) ferric, in which it is trivalent.

Ferrous Compounds

The hydrated Fe^{++} ion (possibly, $\text{Fe}^{++}\cdot 6\text{H}_2\text{O}$) is green, and resembles the manganous ion in many respects.

Soluble and Insoluble Compounds.—The ferrous ion forms soluble salts with most of the common anions, such as FeCl_2 and FeSO_4 . Its most important insoluble salt is the sulfide, FeS .

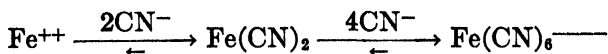
Ferrous Hydroxide.—The Fe^{++} ion combines with the OH^- ion of soluble bases to form $\text{Fe}(\text{OH})_2$. This compound is white, if pure; but it reacts rapidly with the oxygen of the air, turning green, then almost black, and finally red. The constitutions of the intermediate compounds are unknown; the final one is $\text{Fe}(\text{OH})_3$. It follows that $\text{Fe}(\text{OH})_2$ must be a good reducing agent. Alkaline oxidizing agents, such as Na_2O_2 and NaOCl , convert it rapidly into $\text{Fe}(\text{OH})_3$.

Ferrous Sulfide.— Fe^{++} ions combine with S^{--} ions to form black FeS . This is a relatively soluble sulfide, with a solubility of about 4×10^{-10} mole per liter. Its solubility product is therefore approximately 1.6×10^{-19} . Saturated H_2S has an S^{--} concentration of 1.2×10^{-15} , which is sufficient to precipitate Fe^{++} from a *neutral* solution. However the solution becomes acid during the reaction: $\text{Fe}^{++} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}^+$. The result is that the H^+ ions thus formed repress the ionization of the H_2S to the point where the solubility product of FeS is no longer exceeded, so that reaction stops before the precipitation is complete. An alkaline sulfide, such as $(\text{NH}_4)_2\text{S}$, is required completely to precipitate Fe^{++} as FeS . Wet FeS oxidizes readily, forming a basic sulfate.

Ferrous Carbonate.—Alkaline carbonates precipitate white FeCO_3 , soluble in excess H_2CO_3 , forming $\text{Fe}(\text{HCO}_3)_2$ (*cf.* $\text{Ca}(\text{HCO}_3)_2$, page 288). Wet FeCO_3 oxidizes rapidly to $\text{Fe}(\text{OH})_3$.

Ferrous Dimethylglyoxime.—If dimethylglyoxime is added to an Fe^{++} solution containing tartaric acid and NH_4OH is added, a deep red color appears (*cf.* Ni^{++} , page 264). The color fades as the oxidation proceeds. The tartrate prevents the precipitation of $\text{Fe}(\text{OH})_3$. This test for Fe^{++} is very sensitive.

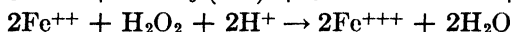
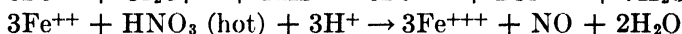
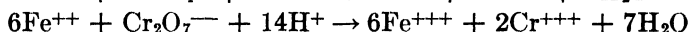
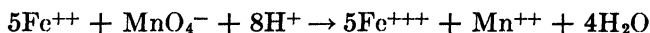
Ferrocyanides.—Soluble cyanides, such as KCN , precipitate from Fe^{++} solution yellow $\text{Fe}(\text{CN})_2$, soluble in excess of the reagent, forming the ferrocyanide ion $\text{Fe}(\text{CN})_6^{--}$.



This complex ion is very stable, dissociating so slightly into Fe^{++}

and CN^- that the usual reagents give no test for Fe^{++} . The $\text{Fe}(\text{CN})_6$ — combines with many cations, forming ferrocyanides of high insolubility, *e.g.*, ferric ferrocyanide (Prussian blue), $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

Reducing Action of Fe^{++} Ions.— Fe^{++} ions in acid solution are readily oxidized to Fe^{+++} by oxidizing agents; *e.g.*,



Ferric Compounds

The Fe^{+++} ion is believed to be colorless. The yellow-to-brown color of ferric solutions may be due to un-ionized molecules or to colloidal $\text{Fe}(\text{OH})_3$ formed hydrolytically. The behavior of this ion is similar to that of the other trivalent cations Al^{+++} and Cr^{+++} .

Soluble and Insoluble Compounds.—Ferric salts of the common anions are generally soluble, though a certain tendency toward hydrolysis is to be noted. The most important insoluble compound is the hydroxide, $\text{Fe}(\text{OH})_3$.

Ferric Hydroxide.— Fe^{+++} ions combine with the OH^- ions of soluble bases, such as NaOH and NH_4OH , forming brown, gelatinous $\text{Fe}(\text{OH})_3$. On ignition, this gives Fe_2O_3 . $\text{Fe}(\text{OH})_3$ is slightly soluble in concentrated NaOH or KOH , possibly owing to a slight amphoteric property. Again, the apparent solubility may be merely peptization. $\text{Fe}(\text{OH})_3$ is quite soluble in certain organic substances containing OH groups, such as glycerin, sugars and tartrates, and cannot be precipitated in their presence.

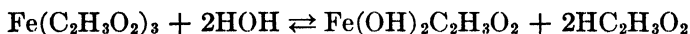
Ferric Carbonate.—The precipitate formed when an alkaline carbonate is added to an Fe^{+++} solution turns out to be $\text{Fe}(\text{OH})_3$, not $\text{Fe}_2(\text{CO}_3)_3$. Alkaline carbonates are partially hydrolyzed, forming OH^- ions; and Fe^{+++} unites with the latter, for $\text{Fe}(\text{OH})_3$ is more insoluble than $\text{Fe}_2(\text{CO}_3)_3$.

Ferric Sulfide.—When an alkaline sulfide, such as $(\text{NH}_4)_2\text{S}$, is added to an Fe^{+++} solution, the precipitate is Fe_2S_3 , and not $2\text{FeS} + \text{S}$, as was formerly supposed. This composition is shown by certain reactions of the precipitate. For example, when Fe_2S_3 is treated with $\text{Zn}(\text{NH}_3)_4(\text{OH})_2$ solution out of contact

with the air, brown $\text{Fe}(\text{OH})_3$ is formed. The product with FeS-S mixtures is white $\text{ZnS} + \text{S}$. However, when Fe_2S_3 is dissolved in HCl , the iron appears as Fe^{++} : $\text{Fe}_2\text{S}_3 + 4\text{H}^+ \rightarrow 2\text{Fe}^{++} + \text{S} + 2\text{H}_2\text{S}$. Evidently Fe^{+++} is reduced by H_2S but not by S^{--} .

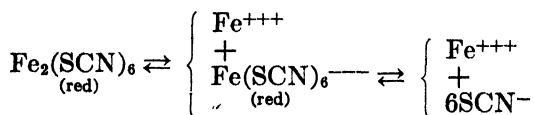
Ferric Phosphate.—Soluble phosphates precipitate Fe^{+++} as yellowish white FePO_4 . FePO_4 is easily soluble in strong acids but insoluble in $\text{HC}_2\text{H}_3\text{O}_2$. It is also soluble in an excess of PO_4^{--} , owing to the formation of a complex anion, possibly $\text{Fe}(\text{PO}_4)_2^{--}$. Evidence of this reaction is found in the bleaching of FeCl_3 solution by PO_4^{--} .

Ferric Acetates.—Alkaline acetates form with cold Fe^{+++} solutions a red-brown color, believed to be due to the normal acetate, $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$. Upon boiling, a brown basic acetate separates, with the approximate formula $\text{Fe}(\text{OH})_2\text{C}_2\text{H}_3\text{O}_2$.

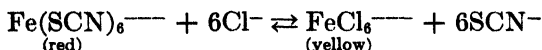


Upon cooling, this precipitate tends to go back into solution. Many organic hydroxy compounds prevent the precipitation of the basic acetate.

Ferric Thiocyanate.— Fe^{+++} solutions form with NH_4SCN or KSCN a deep red color, formerly assumed to be due to the molecule $\text{Fe}(\text{SCN})_3$. More recently it has been proposed that the color is that of the complex anion $\text{Fe}(\text{SCN})_6^{--}$. Ferric thiocyanate is fairly well ionized, and upon electrolysis the red color moves toward the anode. This may be explained by assuming that the molecule is $\text{Fe}_2(\text{SCN})_6$, not $\text{Fe}(\text{SCN})_3$, and that it undergoes stepwise ionization as follows:



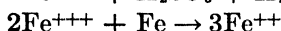
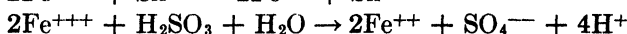
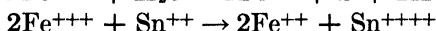
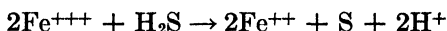
The bleaching of the color by Cl^- , F^- , PO_4^{--} , $\text{C}_2\text{O}_4^{--}$, $\text{C}_4\text{H}_4\text{O}_6^{--}$, etc., is due to tying up the Fe^{+++} ions in other stable complexes; *e.g.*,



Hg^{++} ions decolorize the solution by removing the SCN^- ions as un-ionized $\text{Hg}(\text{SCN})_2$.

Ferric Oxalate.—Oxalates give no precipitate with Fe^{+++} solutions. Probably this is another case of formation of a molecule or ion of low ionization.

Oxidizing Action of Fe^{+++} Ions.— Fe^{+++} ions are reduced to Fe^{++} by H_2S , Sn^{++} , H_2SO_3 , HI , and the metals that liberate hydrogen from dilute acids. For example,



Summary of Tests.—The most important confirmatory tests for Fe^{++} and Fe^{+++} are tabulated as follows:

Reagent	Fe^{++} ions	Fe^{+++} ions
NH_4OH	$\text{Fe}(\text{OH})_2$, green ¹	$\text{Fe}(\text{OH})_3$, brown
SCN^-	$\text{Fe}(\text{SCN})_6^{--}$, red
$\text{Fe}(\text{CN})_6^{--}$	$\text{Fe}_2\text{Fe}(\text{CN})_6$, white ²	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, blue
$\text{Fe}(\text{CN})_6^{--}$	$\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$, blue	$\text{Fe}[\text{Fe}(\text{CN})_6]$, brown
Dimethylglyoxime.....	Red color	

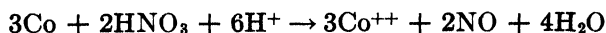
¹ Green instead of white, owing to slight oxidation.

² Usually a light blue color, owing to partial oxidation.

COBALT

The Metal.—Cobalt is a hard, gray metal, resembling iron in a general way. It is used in making very hard steels, such as stellite. Its compounds, besides their use in pure chemistry, are chiefly used in ceramics to give a blue color to glazes.

Cobalt dissolves slowly in warm HCl and in warm dilute H_2SO_4 , with the liberation of H_2 : $\text{Co} + 2\text{H}^+ \rightarrow \text{Co}^{++} + \text{H}_2$. It dissolves more rapidly in dilute HNO_3 .



Concentrated HNO_3 dissolves it very slowly, apparently owing to a passivity effect.

Ions.—The only simple ion formed by cobalt of analytical importance is the cobaltous ion Co^{++} . When associated with six molecules of water of hydration, it becomes the pink $\text{Co} \cdot 6\text{H}_2\text{O}^{++}$ ion. The anhydrous form Co^{++} is probably blue. Cobalt is

trivalent in certain insoluble compounds, such as $\text{Co}(\text{OH})_3$, and in certain stable complexes, such as the cobaltinitrite ion $\text{Co}(\text{NO}_2)_6^{--}$. The Co^{+++} ion is unstable; if it exists at all, it is in small concentrations only.

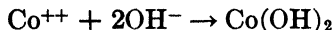
Soluble and Insoluble Compounds.—The salts formed by Co^{++} with the anions of the common acids are soluble—*e.g.*, the chloride, nitrate, sulfate, etc. The most important of the insoluble compounds are cobaltous sulfide, CoS , and cobaltic hydroxide, $\text{Co}(\text{OH})_3$.

Cobalt Sulfide.— Co^{++} ions are not precipitated by H_2S in acid solution but are thrown down in ammoniacal solution by $(\text{NH}_4)_2\text{S}$ as black CoS . An anomalous situation is found in the fact that, while CoS cannot be precipitated in acid solution, when once formed it is practically insoluble in dilute HCl and dilute H_2SO_4 . Two theories have been proposed to explain this strange behavior: (1) Some have suggested that CoS exists in two forms, one soluble in dilute acids and the other insoluble. The soluble form, immediately after its precipitation, goes over into the insoluble form. (2) A much more probable explanation is that there is only one form, which dissolves slowly in dilute HCl . X-ray examination indicates the existence of a single form.

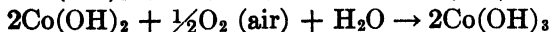
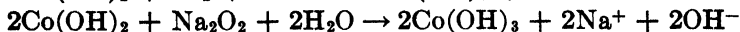
Cobaltous Hydroxide.—Strong bases, such as NaOH solution, precipitate Co^{++} ions in the cold as a blue basic salt; *e.g.*,



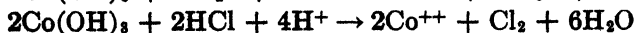
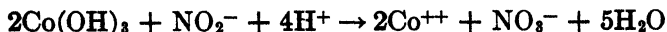
When the reaction mixture is warmed, the pink hydroxide is obtained.



Cobaltic Hydroxide.—Alkaline oxidizing agents convert $\text{Co}(\text{OH})_2$ into $\text{Co}(\text{OH})_3$.



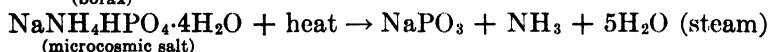
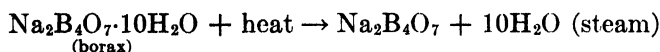
[*Cf.* $\text{Fe}(\text{OH})_2$ and $\text{Mn}(\text{OH})_2$.] $\text{Co}(\text{OH})_3$ is insoluble in acids unless a reducing agent is present.



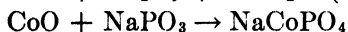
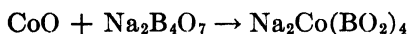
$\text{Co}(\text{H}_2\text{O})_6^{++}$ and the blue color to a compound anion containing four coordinate atoms or groups [*e.g.*, CoCl_4^{--} or $\text{Co}(\text{SCN})_4^{--}$].

This latter hypothesis is supported by considerable chemical and physical evidence: (1) Upon electrolysis, the pink constituent moves toward the cathode, and the blue one toward the anode. (2) The blue color is changed to pink by anhydrous ZnCl_2 , although it is a powerful dehydrating agent. Presumably the zinc displaces the cobalt from CoCl_4^{--} , giving ZnCl_4^{--} and Co^{++} . HgCl_2 has a similar effect. (3) Changes in viscosity and density are easily explained in terms of shifts in the equilibrium $\text{Co}^{++} + 4\text{Cl}^- \rightleftharpoons \text{CoCl}_4^{--}$.

Bead Reactions.—When a cobalt compound is heated with a borax or a metaphosphate bead, a blue color is obtained. These beads are formed by heating borax or microcosmic salt on a loop of platinum wire.



Cobalt salts, when heated in the oxidizing flame, form CoO , which dissolves in these beads, probably forming mixed borates and phosphates.



The blue color is usually explained as due to the formation of anhydrous salts. In the case of the borate bead, the explanation of an anion radical containing four coordinate groups is also possible. The case of the phosphate is not so easily explained.

Detection.—The following reactions are used in detecting the Co^{++} ion: (1) A Co^{++} solution gives a blue color when treated with concentrated HCl . (2) NH_4SCN gives a blue¹ color with a concentrated solution of Co^{++} , soluble in amyl alcohol-ether mixture. (3) Dimethylglyoxime forms a brown solution with Co^{++} ions. This test is not reliable in the presence of Ni^{++} ions. (4) Concentrated KNO_2 solution in the presence of $\text{HC}_2\text{H}_3\text{O}_2$ precipitates yellow $\text{K}_3\text{Co}(\text{NO}_2)_6$ (Fischer's salt), sometimes forming

¹ Fe^{+++} ions interfere with this test by forming red $\text{Fe}(\text{SCN})_6^{--}$. This may be decolorized by the addition of a tartrate, such as $\text{KNaC}_4\text{H}_4\text{O}_6$.

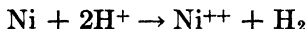
slowly. (5) Cobalt compounds give a blue color with borax and metaphosphate beads.

Tests with Organic Reagents.—In addition to the preceding, the following tests have been proposed: (1) α -Nitroso- β -naphthol gives with Co^{++} a purple-red precipitate, $\text{Co}(\text{C}_{10}\text{H}_6(\text{NO})\text{O})_3$, insoluble in HCl ; Cu^{++} and Fe^{+++} ions interfere. (2) When Co^{++} ions are mixed with nitroso-R-salt in $\text{HC}_2\text{H}_3\text{O}_2\text{-NaC}_2\text{H}_3\text{O}_2$ solution and then heated with concentrated HNO_3 , a red solution is formed. Fe^{++} ions interfere by giving a red color, and Ni^{++} by giving a brown color. (3) Resorcinol in NH_4OH forms with Co^{++} upon heating a blue-violet solution, which turns red upon acidification.

NICKEL

The Metal.—Nickel is a hard, white metal, decidedly resistant to corrosion. It is used in alloy steels, in Monel metal (Ni , Cu) and German silver (Cu , Zn , Ni), in the resistance alloys used in electrical heaters, and in coinage. On account of its hardness and resistance to corrosion, it is used in electroplating other metals. The use of nickel compounds is almost wholly industrial—mainly in electroplating baths.

Metallic nickel is slowly soluble in HCl and in dilute H_2SO_4 , forming Ni^{++} and free H_2 . It dissolves more rapidly in dilute HNO_3 .



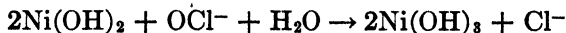
Nickel is insoluble in concentrated HNO_3 , owing to a passivity effect.

The Ion.—Nickel forms a single simple cation—the green divalent nickelous ion $\text{Ni}(\text{H}_2\text{O})_6^{++}$. The six molecules of water of hydration seem to be responsible in some way for the green color. The anhydrous ion is usually considered to be brown. Nickel is trivalent in a few compounds, such as $\text{Ni}(\text{OH})_3$ and Ni_2O_3 —all insoluble in water. Hence the nickelic ion Ni^{+++} is unknown.

Solubilities.—The nickelous salts are generally soluble, *e.g.*, the chloride, nitrate, sulfate, acetate, etc. The most important of the insoluble compounds are the sulfide, the dimethylglyoxime derivative, the hydroxide, and the oxide.

Nickel Hydroxides.— Ni^{++} ions are precipitated by OH^- ions as green nickelous hydroxide, $\text{Ni}(\text{OH})_2$. Upon ignition, $\text{Ni}(\text{OH})_2$

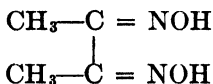
goes over into the green oxide, NiO . Ni(OH)_2 is not so easily oxidized as Co(OH)_2 . Even Na_2O_2 will not convert it into Ni(OH)_3 , though sodium hypochlorite will.



Some authorities consider the product a hydrated dioxide, as $\text{NiO}_2 \cdot \text{H}_2\text{O}$. In acid solution, it is a strong oxidizing agent.

Nickel Ammonia Complex Ions.— Ni^{++} ions add NH_3 , forming a series of nickeloammines. The limit ammine of the series is the hexammine $\text{Ni(NH}_3)_6^{++}$, and it is generally considered the normal product. It is deep blue in color, resembling $\text{Cu(NH}_3)_4^{++}$, though the color is not so intense. These NH_3 complex ions are only moderately stable and react readily with ions that form compounds of high insolubility— NiS , for example.

Glyoxime Derivatives.—In 1883, Schramm prepared a new organic compound, called *dimethylglyoxime*,¹ having the composition



This compound acts as a weak monobasic acid, one of the NOH groups functioning as an acid group. In 1905, the Russian chemist Tschugaeff discovered that dimethylglyoxime forms a bright-red salt with Ni^{++} , having the composition $\text{Ni(C}_4\text{H}_7\text{N}_2\text{O}_2)_2$. This salt forms in either weak acid or ammonia solution, and the reaction is sensitive enough to detect 1 part of Ni^{++} in 400,000 parts of solution. The only interfering cation is ferrous, Fe^{++} . Certain other organic dioximes give similar reactions.

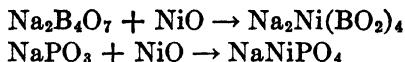
Nickel Sulfide.—Nickel sulfide is similar to cobalt sulfide in its preparation and properties, including its slow solubility in HCl . It differs in one respect, *viz.*: it is peptized by $(\text{NH}_4)_2\text{S}_x$, forming a brown colloid that runs through the filter. Opinion is divided as to whether the colloid is a simple sulfide, NiS , or a polysulfide, NiS_x . It may be precipitated by acidifying with $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$ and boiling.

Nickel Thiocyanate.—The reaction between Ni^{++} and SCN^- ions seems to parallel that of Co^{++} and SCN^- , with the difference

¹ Recently the name *diacetyl dioxime* has been proposed as representing the composition more correctly.

that $\text{Ni}(\text{SCN})_4$ — is practically colorless. The Vogel test, therefore, is only a test for Co^{++} and not a method of separation.

Borax and Metaphosphate Bead Tests.—Nickel oxide dissolves in fused borax and sodium metaphosphate, possibly forming complex salts.



These melts are colorless when hot but turn brown upon cooling. Since many other metallic oxides form colored beads, the reactions are valuable mainly as confirmatory tests.

Detection.—The presence of Ni^{++} may be shown more or less definitely during an analysis by the following reactions: (1) a green color in the Group III solution (in the absence of Cr^{+++} and Fe^{++}); (2) a deep blue color in the NH_4OH solution (in the absence of H_2S); (3) a black sulfide, apparently insoluble in dilute HCl (in the absence of Co^{++}); and (4) a brown filtrate from the precipitation of Group III by means of $(\text{NH}_4)_2\text{S}$.

The most sensitive and reliable test for Ni^{++} is the formation of a red precipitate with dimethylglyoxime. The borax and metaphosphate bead tests are sometimes used.

Tests with Organic Reagents.—In addition to those described in the preceding paragraph, Ni^{++} ions give the following reactions with organic agents: (1) α -nitroso- β -naphthol gives with Ni^{++} a brown precipitate, soluble in HCl ; (2) dicyandiamidine sulfate gives a yellow crystalline precipitate in an ammoniacal solution containing NH_4^+ salts.

ANALYSIS

There are several procedures for the analysis of Group III. Each has its advantages, depending on the composition of the solution. Unfortunately, in many cases, the best procedure cannot be known until after the analysis is completed.

Precipitation.—Valuable information about the composition of a Group III solution can be obtained by carrying out the precipitation in steps. First, NH_4OH is added, and its effects noted. Next, H_2S is added, and its effects noted. An interpretation of these reactions (Table 28) may indicate definitely the absence of one or more members of the group.

If the solution has been previously treated with H_2S , the reactions of the NH_4OH will be masked by $(\text{NH}_4)_2\text{S}$ reactions. For

this reason, before the NH_4OH is added, the acid solution is boiled until the absence of H_2S is shown by testing the vapors with $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ paper.

TABLE 28.—THE REACTIONS OF GROUP III IONS WITH NH_4OH AND $(\text{NH}_4)_2\text{S}$

Ion	NH_4OH	$\text{NH}_4\text{OH} + \text{H}_2\text{S}$
Al^{+++}	$\text{Al}(\text{OH})_3$, white gel	$\text{Al}(\text{OH})_3$
Cr^{+++}	$\text{Cr}(\text{OH})_3$, green gel	$\text{Cr}(\text{OH})_3$
Zn^{++}	$\text{Zn}(\text{NH}_3)_4^{++}$, colorless	ZnS , white
Mn^{++}	MnS , salmon
Fe^{++}	$\text{Fe}(\text{OH})_2$, green \rightarrow dark \rightarrow red	FeS , black
Fe^{+++}	$\text{Fe}(\text{OH})_3$, red-brown	Fe_2S_3 , black
Co^{++}	$\text{Co}(\text{NH}_3)_6^{++}$, yellow-red	CoS , black
Ni^{++}	$\text{Ni}(\text{NH}_3)_6^{++}$, deep blue	NiS , black

1. Chromium should be present in the Group III solution as Cr^{+++} and not CrO_4^{--} or $\text{Cr}_2\text{O}_7^{--}$; and manganese as Mn^{++} and not MnO_4^- . CrO_4^{--} ions are not precipitated by $(\text{NH}_4)_2\text{S}$, and MnO_4^- ions give a mixture of MnS and MnO_2 . In order to avoid these complications, either the solution should be a filtrate from a Group II precipitation, or else it should have been previously saturated with H_2S in the presence of dilute HCl .

2. The solution should contain a sufficient concentration of NH_4^+ ions to prevent the precipitation of $\text{Mg}(\text{OH})_2$. On the other hand, an excess must be avoided, for high concentrations of NH_4^+ interfere with the precipitation of Group IV. If the solution is a filtrate from a Group II precipitation, a sufficient concentration of NH_4^+ will have been introduced by neutralizing the 4 cc. of 6 *M* HCl by NH_4OH . If the solution is not a filtrate from Group II, about 5 cc. of 2 *M* NH_4Cl should be added before introducing the NH_4OH .

3. The NH_4OH should be added slowly, a large excess being carefully avoided. $\text{Al}(\text{OH})_3$ is sufficiently soluble in high concentrations of NH_4OH for part of it to pass into Groups IV and V where it may cause serious errors.

4. Sometimes the filtrate from the Group III precipitation is not colorless. A yellow color is due to the presence of polysulfide ions S_x^{--} , formed by atmospheric oxidation of $(\text{NH}_4)_2\text{S}$. A brown color is due to colloidal NiS , formed by the action of Ni^{++} and S_x^{--} ions. A pink color may be due to an ammonia chromium complex ion, probably $\text{Cr}(\text{NH}_3)_6^{+++}$. High concentrations of NH_4^+ ions favor the formation of this complex.

5. The filtrate from Group III should be promptly acidified and boiled, in order to expel H_2S . The S^{--} ion is rapidly oxidized by the air to SO_4^{--} , which precipitates Ba^{++} and Sr^{++} in forms that do not respond to the Group IV treatment. This procedure precipitates any colloidal NiS and S , which should be filtered out at once. The Ni^{++} in the precipitate may be detected

by extracting the residue with warm dilute HNO_3 and adding NH_4OH and dimethylglyoxime.

Separation into Subgroups.—The ions of Group III show a variety of reactions, so that a number of analytical procedures are possible. However, the division of the group into subgroups is usually based upon one or more of the following reactions: (1) CoS and NiS are practically insoluble in dilute HCl (*i.e.*, they dissolve slowly), whereas the sulfides and hydroxides of the other members of the group dissolve readily. (2) Excess NaOH precipitates Mn^{++} , Fe^{+++} , Co^{++} , and Ni^{++} as insoluble hydroxides but redissolves the amphoteric hydroxides $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, and $\text{Zn}(\text{OH})_2$. (3) The combination $\text{NaOH} + \text{Na}_2\text{O}_2$ gives the same separation as NaOH , but certain of the ions are oxidized to higher valences. (4) NH_4OH precipitates Al^{+++} , Cr^{+++} , and Fe^{+++} as hydroxides, leaving the other members in solution as simple ions or their ammonia complexes.

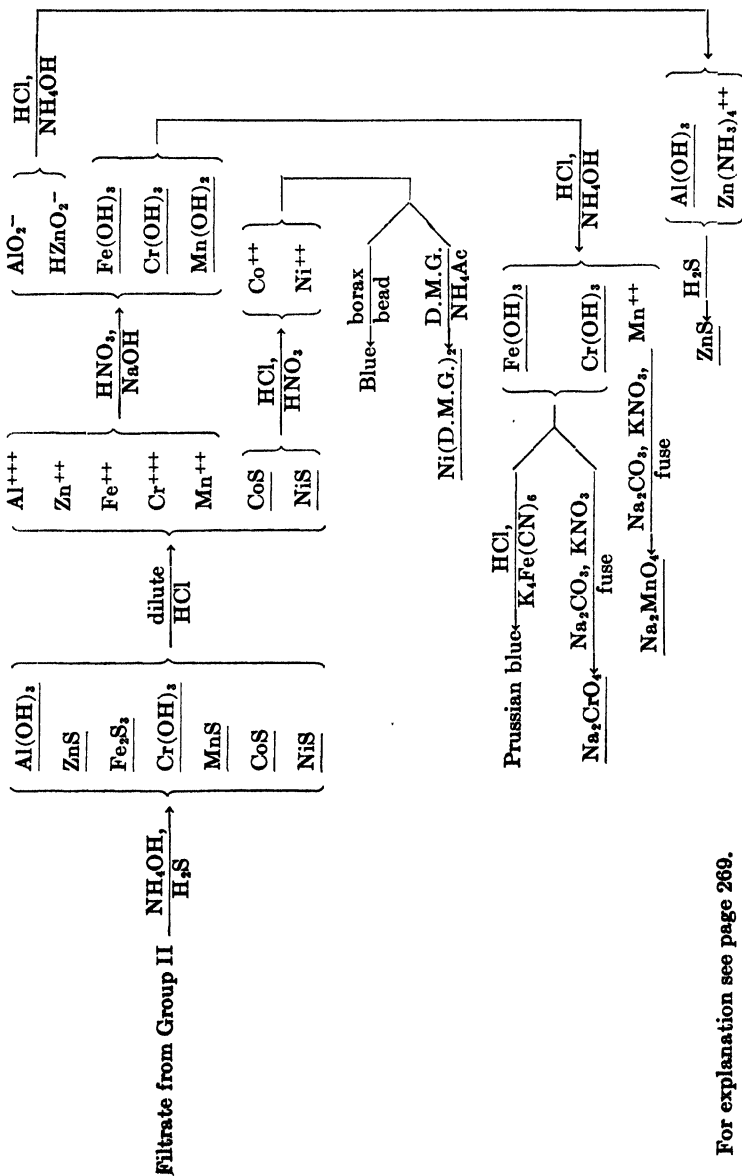
The most common of the procedures are given in the following paragraphs.

The Sulfide-hydroxide Method.—A procedure frequently used involves the separation of CoS and NiS by their slow solubility in dilute HCl , and the separation of $\text{Mn}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ by precipitation with NaOH . This procedure is outlined in Table 29.

The NaOH - Na_2O_2 Method.—In 1897, Professor S. W. Parr of the University of Illinois proposed the use of a combination of NaOH and Na_2O_2 as the reagent for separating the Aluminum and Iron subgroups. The Na_2O_2 * converts the mischievous $\text{Cr}(\text{OH})_3$ into CrO_4^{--} , which remains soluble and shows no tendency to form insoluble compounds with any of the members of Group III. Though the membership of these subgroups remains unchanged, the composition of the ions and precipitates is different in several cases.

Aluminum Subgroup	Iron Subgroup
AlO_2^-	MnO_2
CrO_4^{--}	$\text{Fe}(\text{OH})_3$
HZnO_2^-	$\text{Co}(\text{OH})_3$
	$\text{Ni}(\text{OH})_2$

* Sodium peroxide is a powerful oxidizing agent, capable of igniting paper, towels, etc. For this reason, it should never be stored in desks, and any excess should be put in the sink (not the waste jar).

TABLE 29.—THE CoS-NiS-NaOH METHOD

For explanation see page 269.

Except in the case of Cr^{+++} , the oxidation effects are altogether incidental. It makes no difference in the course of the analysis whether the elements involved are in the oxidized or the reduced form.

The usual procedure in the analysis of these subgroups is outlined in Table 30.

The $\text{NH}_4\text{OH}-(\text{NH}_4)_2\text{S}$ Procedure.—As stated on page 240, some textbooks divide Group III, as represented in this book, into two major groups called the *Ammonium Hydroxide group* and the *Ammonium Sulfide group*. The first group is precipitated by NH_4OH from the filtrate from Group II, after boiling out any H_2S . The second group is precipitated by the action of H_2S on the ammoniacal filtrate. The membership of this group is therefore as follows:

The NH_4OH group: Al^{+++} , Cr^{+++} , Fe^{+++}

The $(\text{NH}_4)_2\text{S}$ group: Zn^{++} , Mn^{++} , Co^{++} , Ni^{++}

The analysis of the two groups is outlined in Table 31.

Procedure in the Presence of Phosphates and Oxalates.—There are a number of anions that form salts with Ca^{++} , Sr^{++} , Ba^{++} , and Mg^{++} , which are soluble in acids, but are reprecipitated upon making the solution basic. In the presence of these anions, the cations of Group IV and Mg^{++} are precipitated prematurely when the solution is made alkaline by NH_4OH in the precipitation of Group III. Their presence in Group III would interfere with the analysis of the Iron subgroup; further, they might not be detected in their regular places in the analytical scheme and would therefore be reported as absent.

The following anions might be involved in this complication: phosphate, oxalate, fluoride, borate, tartrate, and several other

1. The separation of Co^{++} and Ni^{++} by means of the insolubility of their sulfides in dilute HCl is not "clean." Small amounts go into solution, and usually "come out" along with the Mn^{++} , but give slight interference in the detection of this ion.

2. $\text{Cr}(\text{OH})_3$ seems to form an insoluble chromite with Zn^{++} —possibly $\text{Zn}(\text{CrO}_2)_2$. The result is that Zn^{++} is carried down by the $\text{Cr}(\text{OH})_3$, and tends to reappear later, usually along with the Mn^{++} . This loss weakens the detection of Zn^{++} in its regular place.

3. The confirmatory tests for the precipitates obtained may be varied *ad libitum*.

TABLE 30.—THE $\text{NaOH-Na}_2\text{O}_2$ METHOD

Filtrate from Group II $\xrightarrow[\text{H}_2\text{S}]{\text{NH}_4\text{OH}}$			
Al(OH)_3	Al^{+++}	AlO_2^-	$\text{HCl, NH}_4\text{OH}$ boil
Cr(OH)_3	Cr^{+++}	CrO_4^{--}	
ZnS	Zn^{++}	HZnO_2^-	
MnS	Mn^{++}	MnO_2	
FeS	Fe^{+++}	Fe(OH)_3	HNO_3
CoS	Co^{++}	Co(OH)_3	NaNO_2
NiS	Ni^{++}	Ni(OH)_2	
$\xrightarrow[\text{H}_2\text{S}]{\text{NaOH, Na}_2\text{O}_2}$			
Fe(OH)_3	NH_4OH	$\text{HNO}_3, \text{KClO}_3$ boil	Mn^{++}
$\text{Co(NH}_3)_6^{++}$			Fe^{+++}
$\text{Ni(NH}_3)_6^{++}$			Co^{++}
$\xrightarrow[\text{HCl, NH}_4\text{SCN}]{\text{HCl, NH}_4\text{SCN}}$			
Co(SCN)_4^{--}			
$\xrightarrow[\text{HAc, D.M.G.}]{\text{HAc, D.M.G.}}$			
Ni(D.M.G.)_2			
BaCrO_4	BaAc_2	Al(OH)_3	
ZnS	H_2S	CrO_4^{--}	
Zn^{++}		$\text{Zn(NH}_3)_4^{++}$	

For explanation see page 271.

organic acid groups. Of these anions, all except phosphate and oxalate are removed from the unknown during the evaporation with HNO_3 , in regulating the acidity just before the precipitation of Group II. Oxalate may also be removed, but usually this action is not complete. Arsenate would also precipitate these cations in Group III, were it not completely removed as sulfide in Group II.

The underlying principle in the procedure is (1) to test for these anions and (2) to remove them if present. Then (3) a second precipitation of Group III will be carried out, and (4) the filtrate will be analyzed for Ca^{++} , Sr^{++} , Ba^{++} , and Mg^{++} in the regular way. This filtrate must not be added to the filtrate from the first Group III precipitate, for the second filtrate now contains

1. The filtrate from Group II is boiled to expel H_2S , and then NH_4OH is added and its reaction in the absence of H_2S noted and interpreted. No precipitate shows the absence of Al^{+++} , Cr^{+++} , Fe^{+++} , and the complicating phosphates and oxalates of the alkaline earth group. A blue solution indicates Ni^{++} , and a reddish one Co^{++} .

2. When the Group III precipitate is treated with dilute HCl alone, a black residue, soluble in aqua regia, indicates Ni^{++} or Co^{++} , or both.

3. An excess of NaOH should be avoided. The hydroxides of Fe^{+++} , Co^{++} , and Ni^{++} are feebly amphoteric, and concentrated NaOH dissolves enough of them to interfere with the tests for Al^{+++} and Zn^{++} .

4. For a similar reason, excess of Na_2O_2 should be avoided. Furthermore, excess Na_2O_2 requires longer boiling for its decomposition.

5. The solution of the Aluminum subgroup should be thoroughly boiled to decompose any excess Na_2O_2 . Upon acidification, Na_2O_2 forms H_2O_2 , which reduces CrO_4^{--} to Cr^{+++} , thereby spoiling the confirmatory test for CrO_4^{--} .

6. A white precipitate obtained when $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ is added is due to SO_4^{--} , formed by the oxidation of S^{--} by air and by peroxides.

7. A yellow color in the solution of the Aluminum subgroup is strongly indicative of CrO_4^{--} . Other possibilities are polysulfides and Fe^{+++} , the presence of both being possible only through faulty technique.

8. Peroxides, unless decomposed by boiling, will react with H_2S , forming a precipitate of white sulfur. This may be mistaken for a test for ZnS .

9. The oxidation of Mn^{++} to MnO_2 by HClO_3 proceeds slowly. Excessive amounts of KClO_3 hasten it only slightly, to say nothing of loading the solution with potassium salts.

10. The $\text{Fe}(\text{OH})_3$ precipitate should be thoroughly washed, since traces of oxidizing agents contained in it cause a fading of the $\text{Fe}(\text{SCN})_6^{--}$ color.

11. The presence of Co^{++} may be indicated by a deep blue color whenever the hydrochloric acid solution is concentrated to a small volume.

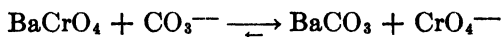
TABLE 31.—THE $\text{NH}_4\text{OH}-(\text{NH}_4)_2\text{S}$ METHOD

Filtrate from Group II	Al^{+++}	$\text{Al}(\text{OH})_3$	$\text{NaOH},$ Na_2O_2	AlO_2^-	$\text{NH}_4\text{Cl},$ boil	$\text{Al}(\text{OH})_3$ CrO_4^{--}
	Cr^{+++}	$\text{Cr}(\text{OH})_3$		CrO_4^{--}		
	Fe^{+++}	$\text{Fe}(\text{OH})_3$		$\text{Fe}(\text{OH})_3$		
	Mn^{++}	Mn^{++}		MnS		
	Zn^{++}	$\text{Zn}(\text{NH}_3)_4^{++}$	H_2S	ZnS	HCl	
	Co^{++}	$\text{Co}(\text{NH}_3)_6^{++}$		CoS		
	Ni^{++}	$\text{Ni}(\text{NH}_3)_6^{++}$		NiS		
		MnO_2	$\text{NaOH},$ Br_2	Mn^{++}		
		$\text{ZnS} \xleftrightarrow{\text{H}_2\text{S}} \text{HZnO}_2^-$		Zn^{++}		
		$\text{Co}(\text{SCN})_4^{--} \xleftarrow{\text{NH}_4\text{SCN}} \text{Co}^{++}$		CoS		
		$\text{Ni}(\text{D.M.G.})_2 \xleftarrow{\text{D.M.G.}} \text{Ni}^{++}$		NiS		
		$\text{Ni}(\text{D.M.G.})_2 \xleftarrow{\text{NH}_4\text{Ac}}$				

For explanation see page 273.

Na^+ and K^+ introduced during the analysis of Group III. These added cations would vitiate the tests for Na^+ and K^+ in Group V. The two filtrates are analyzed separately. Sometimes Ca^{++} , Sr^{++} , Ba^{++} , and Mg^{++} are found in both filtrates, sometimes in only one.

Transposition of BaCrO_4 .—If Ba^{++} is present, it will combine with the CrO_4^{--} , forming insoluble BaCrO_4 . The CrO_4^{--} will in this way be carried into the Iron subgroup, and tests for it in the Aluminum subgroup may be negative. Sr^{++} will also tend to carry CrO_4^{--} into the Iron subgroup, but to a less degree. In order to prevent the loss of CrO_4^{--} from the Aluminum subgroup, Na_2CO_3 is added along with the NaOH and Na_2O_2 , to transpose any BaCrO_4 that might be formed.



This reaction is normally reversible, with the equilibrium point decidedly toward the left-hand side, owing to the greater insolubility of BaCrO_4 . However, with increase of CO_3^{--} the equilibrium will be shifted to the right, and with excess of CO_3^{--} the reaction will be practically complete in that direction.

The relation between the amounts of CrO_4^{--} and CO_3^{--} may be calculated by means of the mass law. The solution is saturated with respect to both BaCrO_4 and BaCO_3 , and hence $[\text{Ba}^{++}]$ is the same for both. Dividing their solubility products,

$$\frac{[\text{Ba}^{++}][\text{CO}_3^{--}]}{[\text{Ba}^{++}][\text{CrO}_4^{--}]} = \frac{1.9 \times 10^{-9}}{2.3 \times 10^{-10}}$$

Canceling $[\text{Ba}^{++}]$, the expression becomes

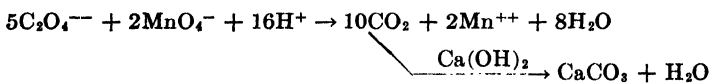
$$\frac{[\text{CO}_3^{--}]}{[\text{CrO}_4^{--}]} = \frac{19}{2.3}, \text{ or } 8$$

1. The principal objection to this procedure is that it is not quantitative in the presence of Cr^{+++} . $\text{Cr}(\text{OH})_3$ carries down Mn^{++} , Zn^{++} and the cations of the alkaline earth groups to a considerable extent, probably as chromites. In the absence of Cr^{+++} , the method is satisfactory. In many cases, the absence of Cr^{+++} is definitely indicated by the absence of a green color in the filtrate from Group II.

2. The separation of Co^{++} and Ni^{++} as sulfides is not clean, but their presence in small amounts in the Mn^{++} - Zn^{++} filtrate causes no serious interference.

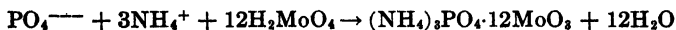
That is, the final concentration of CO_3^{--} ions must be eight times the total concentration of CrO_4^{--} ions. Really 9 moles of Na_2CO_3 must be used for every mole of BaCrO_4 , since 1 gram ion of CO_3^{--} is precipitated as BaCO_3 and therefore is not represented in the final $[\text{CO}_3^{--}]$.

Detection and Removal of Oxalate.—After a small portion of the solution has been tested for Mn^{++} , another portion is tested for $\text{C}_2\text{O}_4^{--}$ by means of acidified KMnO_4 in acid medium.¹ The basis of the test is the oxidation of $\text{C}_2\text{O}_4^{--}$ to CO_2 , which is passed into $\text{Ca}(\text{OH})_2$ solution, with which it forms a white precipitate.

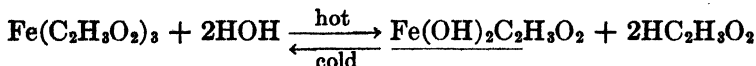


If $\text{C}_2\text{O}_4^{--}$ is found, the remainder of the solution is treated with acidified KMnO_4 in slight excess—i.e., until the pink color persists. The Mn^{++} ions thus introduced must be removed, for they would interfere with the tests for the other cations that might be present. This removal is effected by adding KClO_3 to the solution, strongly acidified with HNO_3 and heated to boiling.

Detection and Removal of Phosphate.—A portion of the solution is tested for PO_4^{--} by warming with $(\text{NH}_4)_2\text{MoO}_4$ - HNO_3 mixture. Its presence is indicated by a yellow precipitate.



If PO_4^{--} ions are found, a portion of the remaining solution is tested for Fe^{+++} ; then excess of FeCl_3 is added, and the mixture is neutralized with NH_4OH . A large volume of 50 per cent $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ is added and the mixture boiled. First of all, the PO_4^{--} is precipitated as FePO_4 , for that has the lowest solubility product of the various possible Fe^{+++} compounds. The remainder of the Fe^{+++} then combines with $\text{C}_2\text{H}_3\text{O}_2^-$ ions, forming red $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$. Upon boiling, hydrolysis takes place, forming insoluble basic ferric acetate.



¹ MnO_2 should not be used instead of KMnO_4 , for it generally contains MnCO_3 . This would give off CO_2 and vitiate the test for $\text{C}_2\text{O}_4^{--}$.

This reaction tends to reverse itself upon cooling, and so the mixture must be filtered while hot.

Separation of Cobalt and Nickel.—The filtrate from the basic acetate precipitation may contain Co^{++} , Ni^{++} , Ba^{++} , Sr^{++} , Ca^{++} , and Mg^{++} , along with Na^+ and K^+ introduced in the reagents, and a large excess of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$. The Co^{++} and Ni^{++} are separated as sulfides by adding NH_4OH and saturating with H_2S . This precipitate is dissolved in aqua regia, and these cations are tested for in the usual way.

Removal of Excess Ammonium Acetate.—The filtrate from CoS and NiS is evaporated to dryness and the residue ignited. This removes the excess $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, which interferes with the precipitation of the Group IV carbonates. The filtrate is then analyzed for Group IV and Mg^{++} in the regular way.

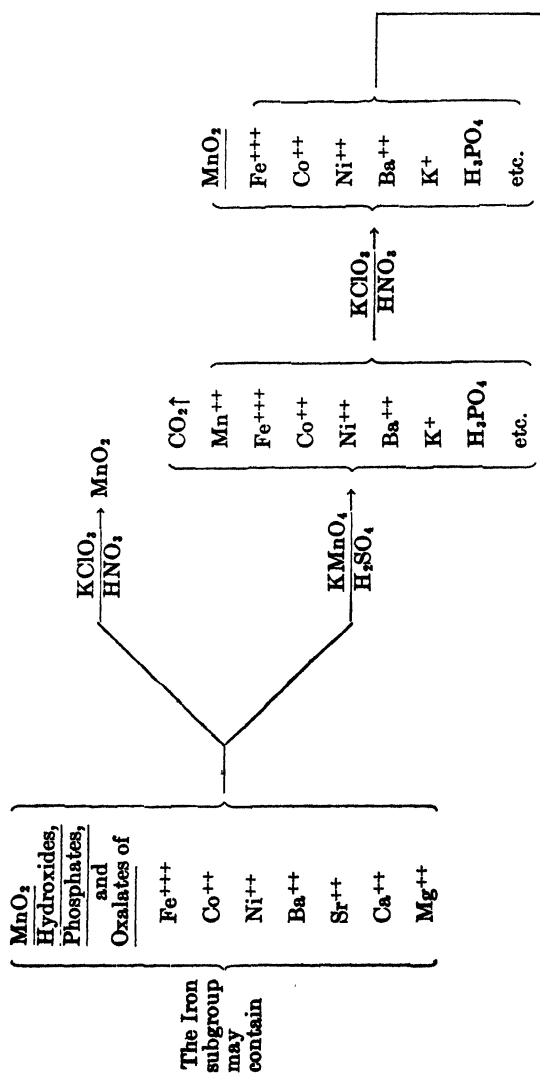
The foregoing procedure is outlined in Table 32.

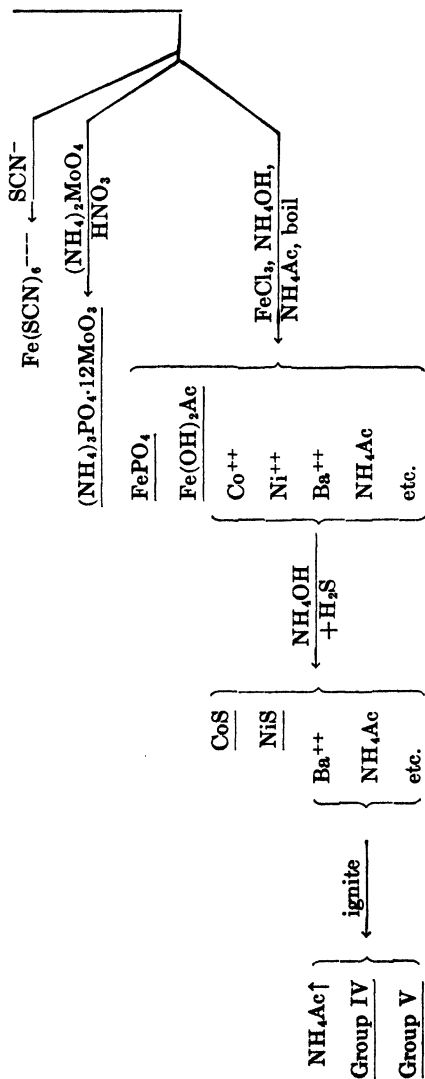
Separation of Aluminum and Zinc.—In the absence of NH_4^+ ions, NH_4OH gives with Zn^{++} ions a white gelatinous precipitate that resembles $\text{Al}(\text{OH})_3$. Error at this point is sometimes met when an attempt is made to test for Al^{+++} on the original solution. In the case of abnormally high concentrations of Zn^{++} ions, such a precipitate may occur even when ordinary amounts of NH_4^+ are present. Such a precipitate, however, fails to give the confirmatory test with aluminon.

Distinction between $\text{Al}(\text{OH})_3$ and H_2SiO_3 .—Strongly alkaline solutions, such as NaOH , attack the glass of reagent bottles, forming soluble Na_2SiO_3 as one of the products. When an acid or an NH_4^+ salt is added, H_2SiO_3 is precipitated in a form that resembles $\text{Al}(\text{OH})_3$. It may be distinguished from $\text{Al}(\text{OH})_3$ in the following ways: (1) It does not form a lake with aluminon. Both H_2SiO_3 and the dye are negative colloids, and for that reason they do not combine. (2) If an acid mixture containing H_2SiO_3 is evaporated to dryness and gently ignited, the H_2SiO_3 is dehydrated, forming SiO_2 , which does not redissolve upon the addition of acid. $\text{Al}(\text{OH})_3$, on the contrary, redissolves and may be reprecipitated by NH_4OH .

The Aluminon Test.—A number of ions interfere with the aluminon test, so that its use on original solutions is questionable. The most frequent interference in the regular analysis is the Fe^{+++} ion. This may be introduced accidentally (e.g., as dust from iron-

TABLE 32.—PROCEDURE IN THE PRESENCE OF PHOSPHATES AND OXALATES





ware) or by the use of too concentrated NaOH solution in separating the Aluminum and Iron subgroups. $\text{Fe}(\text{OH})_3$ is slightly soluble in concentrated NaOH and forms with aluminon a reddish-brown lake. The color is more intense than with $\text{Al}(\text{OH})_3$.

Traces of Al^{+++} may be introduced into analytical solutions from the alumina in pyrex glassware. The amount is always very slight. In case of a questionable test, a blank test may be carried out on the reagents used.

The Perchromic Acid Test.—The H_2O_2 test for CrO_4^{--} is sometimes "tricky," failing in cases where the presence of CrO_4^{--} is definitely indicated by a yellow color in the solution. Since the test is very sensitive, these failures are to be explained either by a loss of the CrO_4^{--} at some point prior to adding H_2O_2 and ether or else by an instant decomposition of the unstable blue liquid. The CrO_4^{--} may be prematurely reduced to Cr^{+++} by the H_2O_2 formed upon acidifying the excess Na_2O_2 used in separating the subgroups. Care should be taken that the boiling is continued several minutes in order to decompose this excess Na_2O_2 . Another source of error is trying to make the test on warm solutions. The heat liberated by neutralizing a strongly alkaline solution with an acid is frequently sufficient to spoil the test.

Another possibility is the reduction of the CrO_4^{--} by the acid used in acidifying the solution. Warm, somewhat concentrated HCl will reduce chromates and thereby spoil the test. Some writers use HNO_3 , but here there is a chance that the NO and NO_2 present in the acid will effect reduction. On the whole, HCl seems preferable, but it should be dilute and should be added to a cold solution.

Separation of Chromate from Zinc.—Chromate ions interfere with the H_2S test for Zn^{++} by precipitating white sulfur, thus: $3\text{H}_2\text{S} + \text{Cr}_2\text{O}_7^{--} + 8\text{H}^+ \rightarrow 3\text{S} + 2\text{Cr}^{+++} + 7\text{H}_2\text{O}$. This interference is conveniently removed by adding $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$, which precipitates CrO_4^{--} as BaCrO_4 . Excess of Ba^{++} ions do not interfere with the test for Zn^{++} .

Frequently a white precipitate, insoluble in acids, is obtained upon adding the $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$. It is BaSO_4 and gives no trouble beyond masking the yellow color of the BaCrO_4 . The SO_4^{--} ions entering into this precipitate come from two sources, *viz.*: the original solution, and the oxidation of sulfur and sulfides to

SO_4^{--} by air and Na_2O_2 . This interference may be reduced, if not completely avoided, as follows: (1) The Group III precipitate is washed promptly with hot water to remove any SO_4^{--} ions normally present in the original solution. (2) The precipitate is then promptly dissolved in HCl or aqua regia, before the sulfides can be oxidized to sulfates by the air. (3) The acid solution thus obtained is filtered to remove any sulfur and boiled to expel any H_2S . If not removed, these materials would be oxidized to SO_4^{--} by the subsequent treatment with Na_2O_2 .

Confirmation of Zinc.—The detection of Zn^{++} ions depends wholly upon tests made after its separation. The most commonly used tests are the following:

1. *Sulfide Test.*— ZnS is thrown down as a white precipitate upon saturating the filtrate from the BaCrO_4 precipitation with H_2S . A possible interference is white sulfur formed by the oxidation of H_2S by (1) H_2O_2 from Na_2O_2 not decomposed by boiling, and (2) $\text{Cr}_2\text{O}_7^{--}$, not precipitated in the preceding step. In such cases, the ZnS should be confirmed by dissolving it in dilute HCl and reprecipitating it by $\text{NH}_4\text{OH} + \text{H}_2\text{S}$.

2. *Ferrocyanide Test.*— Zn^{++} ions are precipitated as white $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ by $\text{K}_4\text{Fe}(\text{CN})_6$. If CrO_4^{--} is not completely removed, a brown coloration will be produced which tends to conceal the presence of the precipitate.

3. *Rinmann's Green Test.*—To get a Rinmann's green test, the solution must be evaporated to dryness with HNO_3 to convert Zn^{++} ions into $\text{Zn}(\text{NO}_3)_2$. This is time consuming, and even then the test is not highly reliable.

Zinc in the Iron Subgroup.—The separation of the Aluminum and Iron subgroups by means of $\text{NaOH} + \text{Na}_2\text{O}_2$ is not "clean." Appreciable amounts of Zn^{++} are carried into the Iron subgroup, especially when Mn^{++} is present. However, the Zn^{++} does not interfere with the analysis of the Iron subgroup, and there is always enough left in the Aluminum subgroup for its detection there. So no attempt is made to retrieve the errant Zn^{++} .

Solution of the Iron Subgroup Precipitate.— MnO_2 and $\text{Co}(\text{OH})_3$ are insoluble in pure (colorless) HNO_3 . A reducing agent, such as NO_2^- ions, is necessary for their solution. In practice, the addition of NO_2^- ions is not necessary in dissolving the subgroup precipitate, for the solution usually contains enough

H_2O_2 from the decomposition of the Na_2O_2 to effect the reduction. In addition, the HNO_3 generally contains NO and NO_2 , which act as reducing agents toward strong oxidizing agents. It follows that the solubility of the subgroup precipitate in HNO_3 is not sufficient evidence for the absence of MnO_2 and $\text{Co}(\text{OH})_3$.

Precipitation of MnO_2 .— MnO_2 is usually precipitated from HNO_3 solution by means of KClO_3 . Apparently the active precipitant is chloric acid, HClO_3 , formed metathetically from KClO_3 and HNO_3 . The precipitation of the MnO_2 is slow and is favored by heat and concentration of both Mn^{++} ions and HNO_3 . Since MnO_2 in acid solution is a strong oxidizing agent, it follows that it will not form if reducing agents (*e.g.*, HCl) are present.

Oxidation of MnO_2 to MnO_4^- .—The formation of a brown precipitate of MnO_2 is a sufficient test for Mn^{++} . However, it is customary to confirm it by oxidizing it to rose-red MnO_4^- by boiling with $\text{PbO}_2 + \text{H}^+$.

Separation and Detection of Fe^{+++} .— Fe^{+++} ions are separated from Co^{++} and Ni^{++} by precipitation as $\text{Fe}(\text{OH})_3$ by NH_4OH . The red-brown color of $\text{Fe}(\text{OH})_3$ is very distinctive, and usually further tests are not necessary.

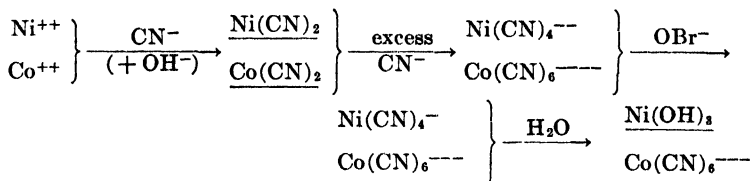
If the $\text{Fe}(\text{OH})_3$ precipitate is not thoroughly washed, it may retain enough NO_3^- and ClO_3^- ions to interfere with the SCN^- test. SCN^- ions are decomposed by strong oxidizing agents, and a large excess of SCN^- may be required to give a permanent red color of $\text{Fe}(\text{SCN})_6^-$. In that respect, the formation of Prussian blue by $\text{K}_4\text{Fe}(\text{CN})_6$ is a more satisfactory test.

Separation of Cobalt and Nickel.—The properties of Co^{++} and Ni^{++} ions are so similar that difficulty in separating them is to be expected. Some of the procedures used are outlined below.

1. *Liebig's Cyanide Method.*—One of the oldest procedures for separating Ni^{++} and Co^{++} is that of Liebig, based upon the instability of trivalent nickel compounds. In alkaline medium, all nickelic compounds are hydrolyzed, forming $\text{Ni}(\text{OH})_3$; in acid solution, they are reduced to nickelous ions Ni^{++} .

If a mixture of Ni^{++} and Co^{++} ions is made basic and an alkaline cyanide added, $\text{Co}(\text{CN})_2$ and $\text{Ni}(\text{CN})_2$ are precipitated. These are soluble in excess CN^- ions, forming the cobaltocyanide ion $\text{Co}(\text{CN})_6^-$ and the nickelocyanide ion $\text{Ni}(\text{CN})_4^-$, respectively. If an oxidizing agent is added— Br_2 , for example—both

elements are oxidized to the trivalent form, presumably giving cobalticyanide, $\text{Co}(\text{CN})_6^{--}$, and nickelicyanide, $\text{Ni}(\text{CN})_4^-$. The nickel complex ion, however, undergoes immediate hydrolysis, forming the brown precipitate $\text{Ni}(\text{OH})_3$; whereas the cobalt remains in solution as the stable $\text{Co}(\text{CN})_6^{--}$. This separation may be represented diagrammatically as follows:



This procedure is *not* satisfactory, particularly in the hands of elementary students.

2. *Glyoxime Methods.*—The above procedure of Liebig's has been replaced by the dimethylglyoxime procedure, which is much simpler and more reliable. In this method, the Ni^{++} is precipitated as red dimethylglyoxime, whereas the Co^{++} forms a brown solution. In the presence of excess Ni^{++} , the formation of the brown soluble Co-dimethylglyoxime is not a sensitive test for Co^{++} , owing to adsorption by the Ni^{++} precipitate.

3. *Precipitation of Potassium Cobaltinitrite.*— KNO_2 , in weakly acid solution, precipitates Co^{++} as $\text{K}_3\text{Co}(\text{NO}_2)_6$ (see page 261). The precipitate forms slowly, especially from dilute solutions. Ni^{++} is not oxidized by HNO_2 , and no potassium nickelinitrite forms.

4. *Other Methods.*—In addition to those already described, a number of other procedures have been proposed, in which organic reagents are used. The following are representative:

Reagent	Co^{++}	Ni^{++}
α -nitroso- β -naphthol.....	Purple red prec., insol. in HCl	Brown prec., sol. in HCl
Dicyandiamine sulfate + NH_4OH + NH_4^+	Red solution	Yellow prec.

As stated on page 265, the extraction of the thiocyanates with alcohol-ether mixture gives no separation of Co^{++} from Ni^{++} . Both pass into the alcohol-ether layer.

Exercises

1. Criticize the definition, "Group III contains the cations that form sulfides soluble in dilute HCl."

2. Why is the precipitation of Group III carried out in the presence of NH_4^+ salts?

3. What members of Group III form complex ions with NH_3 ? Write formulas.

4. What members of Group III form amphoteric hydroxides?

5. What members of Group III may be quantitatively precipitated by NH_4OH ?

6. What members of the group are absent when NH_4OH gives no precipitate with the Group III solution?

7. Do the trivalent cations form carbonates? Explain your answer.

8. Why should yellow ammonium sulfide, $(\text{NH}_4)_2\text{S}_x$, never be used to precipitate Group III?

9. Strictly speaking, is Al_2S_3 an intermediate product in the precipitation of Al^{+++} by $(\text{NH}_4)_2\text{S}$?

10. Name some organic substances that will dissolve $\text{Al}(\text{OH})_3$.

11. How would you explain the failure of Fe_2S_3 to be hydrolyzed? Compare Al_2S_3 , Cr_2S_3 .

12. Explain the brown color obtained when $\text{K}_2\text{Cr}_2\text{O}_7$ solution is saturated with H_2S .

13. In the reaction, $\text{Zn} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{Na}^+ + \text{HZnO}_2^-$, does NaOH act as an acid?

14. Criticize the reaction $3\text{Mn}^{++} + 2\text{HClO}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{MnO}_2 + 2\text{HCl} + 6\text{H}^+$.

15. Write the equation for the oxidation of wet FeCO_3 .

16. What is the effect of acidity and alkalinity upon the following equilibrium: $\text{MnO}_2 + 2\text{H}^+ \rightleftharpoons \text{Mn}^{++} + \text{H}_2\text{O}_2$?

17. Why is NaNO_2 added to a suspension of the Iron subgroup in dilute HNO_3 , just after the separation of the Aluminum subgroup?

18. Under what conditions may the addition of Na_2CO_3 during the separation of the Aluminum and Iron subgroups be omitted?

19. In the analysis of a general unknown, a white Group III precipitate was obtained. List seven possible precipitates.

20. An Iron subgroup precipitate is white and contains PO_4^{---} but no Ba^{++} , Sr^{++} , Ca^{++} , or Mg^{++} . Suggest a possible cation.

21. Describe the results in the Group III analysis of AlPO_4 .

22. In an unknown containing MgNH_4PO_4 and an excess of FeCl_3 , what would be the composition of the Iron subgroup precipitate? Where would the Mg^{++} be found?

23. What would be the objection to testing for Zn^{++} in the presence of $\text{Cr}_2\text{O}_7^{--}$ by means of H_2S ?

24. How would you test for Fe^{++} and Fe^{+++} in the presence of each other?

25. Which of the following cases call for the use of the basic acetate procedure? (a) The Iron subgroup precipitate contains PO_4^{---} but is soluble

in NH_4OH . (b) The Iron subgroup contains PO_4^{---} , along with a large excess of Fe^{+++} , as indicated by the color of the subgroup precipitate. (c) The group III solution contains PO_4^{---} , but there is no Iron subgroup precipitate. (d) NH_4OH gives no precipitate with the Group III solution.

26. Define and illustrate "lake."

27. Name three cations that may be carried down in the Group III precipitate by $\text{C}_2\text{O}_4^{--}$.

28. Show by equilibriums the effect of NH_4^+ salts on the solubility of $\text{Al}(\text{OH})_3$ in NH_4OH .

29. Indicate reagents and principal products in the following separations:

- | | |
|--|--|
| (a) Fe^{+++} and Co^{++} . | (d) Co^{++} and Ni^{++} . |
| (b) Ba^{++} and H_2PO_4 . | (e) PO_4^{---} and AsO_4^{---} . |
| (c) Fe^{+++} and Mn^{++} . | (f) Zn^{++} and Pb^{++} . |

30. What Group III ion makes the use of Na_2O_2 necessary in the separation of the Aluminum and Iron subgroups?

31. Name some of the interferences with the SCN^- test for Fe^{+++} .

32. Suppose a Group III solution containing Al^{+++} , $\text{Cr}_2\text{O}_7^{--}$, Fe^{+++} , Ca^{++} , and PO_4^{---} was treated with excess NH_4OH and then saturated with H_2S . What would become of each ion?

33. Outline the separation of Al^{+++} , Zn^{++} , and Ni^{++} , using as reagents NaOH and NH_4OH .

34. MnO_2 is insoluble in pure HNO_3 , and yet it usually dissolves readily when the Iron subgroup precipitate is treated with HNO_3 . Explain this effect.

35. Identify the following ions of Group III:

(a) A cation that gives no immediate reaction with $\text{NH}_4\text{OH} + \text{NH}_4^+$; the mixture, however, develops a brown precipitate upon standing in contact with the air.

(b) A cation belonging to a later group, whose sulfide is insoluble in water.

(c) A cation that forms a white hydroxide, soluble in excess NH_4OH .

(d) A cation that forms with NaOH a green hydroxide, unaffected by Na_2O_2 .

(e) A cation whose chloride gives a blue solution with concentrated HCl .

(f) A cation giving a brownish precipitate with $\text{K}_3\text{Fe}(\text{CN})_6$, insoluble in HCl .

(g) A cation whose chloride forms a yellow solution, which gives a white precipitate with $\text{H}_2\text{S} + \text{HCl}$.

36. What volume of M NaOH and what weight of Na_2O_2 would be (theoretically) required in carrying out the separation of the Aluminum and Iron subgroups on a solution containing 4 cc. of 0.5 M Al^{+++} , 3 cc. of 0.4 M Mn^{++} , and 2 cc. of 0.3 M Co^{++} . *Ans.*: 8.6 cc. M NaOH , 0.1170 g. Na_2O_2 .

37. There is dissolved 1.962 g. of metallic zinc (at. wt., 65.4) in 15 cc. of 3 M H_2SO_4 . How much 6 M NaOH will it take (a) to make the solution neutral, (b) to precipitate the Zn^{++} as $\text{Zn}(\text{OH})_2$, and (c) to convert the Zn^{++} into HZnO_2^- ?

38. Complete and balance the following equation: $\text{MnO}_2 + \text{NO}_2^- + \text{H}^+ \rightarrow \text{Mn}^{++}$, etc. How many cubic centimeters of M NaNO_2 would be required to dissolve 0.087 g. of MnO_2 (at. wts.: Mn, 55; O, 16).

39. What weight of KClO_3 (mol. wt., 122.5) is needed to precipitate the Mn^{++} from a solution containing 10 cc. of 0.5 M MnCl_2 ? What weight of NaNO_2 (mol. wt., 69) will just redissolve the product? What additional reagents are necessary in each case?

40. Two cubic centimeters of 6 M NH_4OH is added to a neutral solution containing 2 cc. of 0.2 M AlCl_3 , 3 cc. of 0.3 M ZnCl_2 , and 4 cc. of 0.25 M NiCl_2 . What will be the composition of the resultant mixture?

41. What will be the weight of the precipitate obtained by the reaction of an excess of $\text{NH}_4\text{OH} + \text{H}_2\text{S}$ on a solution containing 0.0396 g. of CrCl_3 and 0.054 g. of FeCl_3 ?

42. 1.4 g. of iron (at. wt., 56) is dissolved to form 100 cc. of FeCl_3 solution. How many cubic centimeters of this solution is needed to precipitate the PO_4^{---} in 20 cc. of 0.05 M Na_2HPO_4 to which 5 cc. of 50 per cent $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ has been added?

43. There is dissolved 0.218 g. of zinc in 5 cc. of 3 M H_2SO_4 . How much 6 M NH_4OH and 0.25 M Na_2HPO_4 must be added to precipitate completely the Zn^{++} as ZnNH_4PO_4 ?

44. Calculate the number of moles of $(\text{NH}_4)_2\text{S}$ necessary to precipitate the Group III ion in a solution containing 4 cc. of 0.3 M ZnCl_2 , 2 cc. of 0.5 M $\text{Mn}(\text{NO}_3)_2$, and 3 cc. of M FeSO_4 . What volumes of 6 M NH_4OH and gaseous H_2S (N.T.P.) will be required?

45. What weight of sulfur would be precipitated if an acid solution containing 5 cc. of 0.3 M $\text{K}_2\text{Cr}_2\text{O}_7$ were saturated with H_2S (at. wt. of S, 32)?

46. A solid consists of 0.1534 g. of ZnC_2O_4 and 0.0632 g. of KMnO_4 . What will be the composition of the solution obtained by dissolving it in an excess of dilute HCl (mol. wts.: ZnC_2O_4 , 153.4; KMnO_4 , 157)?

47. A Group III unknown was in the form of a green solution. When NH_4OH was added, the solution first changed to blue and then upon standing became turbid, a brown precipitate finally separating. When this ammoniacal mixture was saturated with H_2S , a buff precipitate was obtained, partially soluble in HCl , leaving a black residue. The precipitate was dissolved in dilute aqua regia, and the solution obtained gave with $\text{NaOH} + \text{Na}_2\text{O}_2$ a dark precipitate and a colorless filtrate. The colorless filtrate was acidified with HNO_3 , and the solution gave with NH_4OH a white precipitate soluble in excess NH_4OH . The dark precipitate was dissolved in $\text{HNO}_3 + \text{KNO}_3$, and the solution gave with KClO_3 a black precipitate, and the filtrate gave with NaOH a green precipitate. What ions are indicated?

48. A Group III unknown was made alkaline with NH_4OH , giving a white precipitate. The mixture was then saturated with H_2S , forming a black precipitate (1). Precipitate (1) was dissolved in dilute aqua regia, and NaOH and Na_2O_2 added, giving a brownish black precipitate (2) in a colorless solution (3). After filtering, the filtrate (3) was made just acid with HCl , and then NH_4OH was added in slight excess, giving a permanent white precipitate. The precipitate (2) was not completely soluble in concen-

trated HNO_3 but dissolved upon the addition of a little NaNO_2 . The resulting solution gave no precipitate upon treatment with KClO_3 . At this point, the solution was divided into three parts. One part was treated with NH_4OH , giving a reddish-brown precipitate. Another portion was treated with $(\text{NH}_4)_2\text{MoO}_4 + \text{HNO}_3$ and warmed, forming a yellow precipitate. The third and largest part of the solution was treated with FeCl_3 , and then an excess of NH_4OH was added. $\text{HC}_2\text{H}_3\text{O}_2$ was added in slight excess, and 5 g. of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ introduced. The solution was then diluted, boiled, and filtered, and the precipitate discarded. The filtrate was treated with H_2S , giving a black precipitate which dissolved in $\text{HCl} + \text{HNO}_3$, giving a pink solution. What ions are indicated?

49. NH_4OH was added to a Group III unknown, giving a greenish white precipitate in a red-yellow solution. Without filtering, the mixture was saturated with H_2S , giving a grayish precipitate. This precipitate was partially soluble in dilute HCl , a little HNO_3 being necessary to dissolve the black residue. When this aqua regia mixture was warmed, it turned blue but became almost colorless upon the addition of water. To this solution, NaOH , Na_2O_2 , and Na_2CO_3 were added, giving a yellow solution (1) and a grayish precipitate (2).

Yellow solution (1) was treated with HCl and NH_4OH without effect. $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution was added, and the cream-colored precipitate discarded. The filtrate from this precipitate was saturated with H_2S , giving a precipitate insoluble in $\text{HC}_2\text{H}_3\text{O}_2$, but soluble in HCl .

Grayish precipitate (2), which was evidently a mixture of white and black materials, was dissolved in $\text{HNO}_3 + \text{NaNO}_2$, and portions of it tested as follows: One portion gave no reaction when KClO_3 was added to the boiling solution; a second portion was treated with $(\text{NH}_4)_2\text{MoO}_4 + \text{HNO}_3$ without effect; the remainder gave with KMnO_4 a colorless gas that turned $\text{Ca}(\text{OH})_2$ milky. To this last solution were added HNO_3 and KClO_3 , this time giving a considerable amount of brown-black precipitate. After filtration through asbestos, this solution gave with NH_4OH a red-brown gelatinous precipitate in a reddish solution.

What ions are indicated?

CHAPTER XVII

GROUP IV—THE AMMONIUM CARBONATE GROUP

The group contains the cations of the alkaline earth family:

Calcium, Ca^{++} Strontium, Sr^{++} Barium, Ba^{++}

Magnesium, Mg^{++} , is also to be included when the group is precipitated in the presence of alcohol.

Characteristics and Reagent.—The characteristics of the group are as follows: The chlorides are soluble in water, and the sulfides are soluble in acids and in NH_4^+ solutions. Hence these ions are not precipitated in Groups I, II, and III. The car-

TABLE 33.—SOLUBILITIES OF GROUP IV PRECIPITATES

	Ba^{++}	Sr^{++}	Ca^{++}	Mg^{++}
CO_3^{--}	0.00012	0.000074	0.00013	0.01
CrO_4^{--}	0.000015	0.0059	1	3
SO_4^{--}	0.00001	0.0004	0.015	2.8
$\text{C}_2\text{O}_4^{--}$	0.00038	0.00024	0.00004	0.0027
OH^-	0.22	0.065	0.022	0.0001

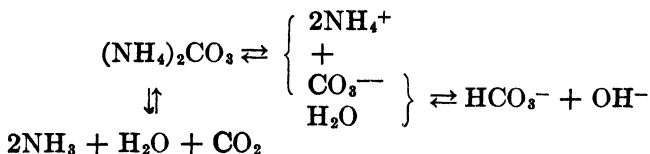
bonates are insoluble in water and only slightly soluble in cold NH_4^+ solutions, so that they may be precipitated by $(\text{NH}_4)_2\text{CO}_3$ in the presence of NH_4^+ . By referring to Table 33, it will be seen that the carbonate is the most uniformly insoluble salt of the group. It will also be noted that MgCO_3 is rather insoluble in water; however, it is readily soluble in solutions containing NH_4^+ salts.

The group reagent is ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, prepared by dissolving technical ammonium carbonate in dilute NH_4OH solution. The solid furnished by the manufacturing chemist is approximately an equimolecular mixture of ammonium hydrogen carbonate, NH_4HCO_3 , and ammonium carbamate, $\text{NH}_4\text{CO}_2\text{NH}_2$. The NH_4OH is added to convert the HCO_3^- into CO_3^{--} . This is important, since the hydrogen carbonates (bicar-

bonates) of this group are soluble. The carbamates are also soluble, and the carbamate ion must be changed into carbonate, as follows:



This change occurs at about 60°. The composition of the reagent may be approximately represented by the following scheme:



The concentration of OH^- is sufficient to repress the last equilibrium very effectively.

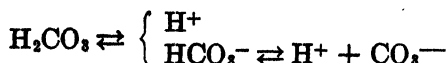
On account of the close resemblances of the elements to each other, they will be considered together and not individually. This will also bring out their differences more sharply.

The Metals.—Calcium, strontium, and barium are active metals, decomposing water slowly at ordinary temperatures. They are used to a small extent in alloys (*e.g.*, certain bearing metals) where they seem to serve more as a “getter” for oxides than as an active component.

The Ions.—The elements of this group form the divalent cations Ca^{++} , Sr^{++} , and Ba^{++} . These ions are colorless and show no tendency to enter into complex formation. It has been suspected that they may form unstable complex ions with NH_3 , but no conclusive evidence is forthcoming.

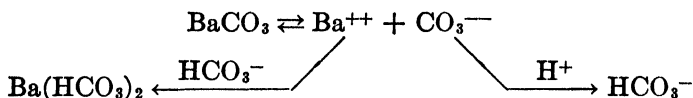
Soluble and Insoluble Salts.—Most of the salts of the group are soluble. The more important insoluble compounds are listed in Table 33.

Carbonates.— Ba^{++} , Sr^{++} , and Ca^{++} form white carbonates, insoluble in water, but soluble in HCl , HNO_3 , and $\text{HC}_2\text{H}_3\text{O}_2$. They are precipitated by alkaline carbonates but not by CO_2 . This is owing to the low ionization of H_2CO_3 . This acid ionizes stepwise as follows:



The secondary ionization, forming CO_3^{--} , is exceedingly small

and does not give sufficient concentration to exceed the solubility products of the carbonates. In order to obtain the requisite CO_3^{--} concentration, the H^+ ions must be removed. Solutions of alkaline earth hydroxides give instant precipitates with CO_2 , for they provide the necessary OH^- ion to remove the H^+ ions. As long as the solution is even slightly acidic, the carbonic acid is present as HCO_3^- and H_2CO_3 . On the other hand, starting with a neutral solution, it is easy to build up an acidity sufficient to tie up the slight concentration of CO_3^{--} coming from the alkaline earth carbonates; *e.g.*,



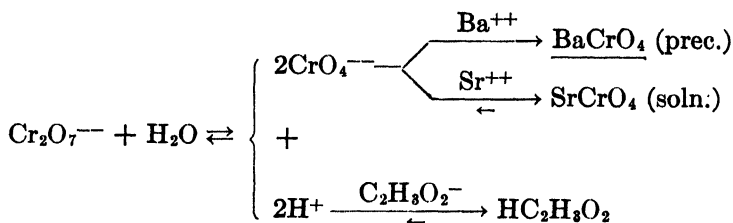
Consequently, if an excess of CO_2 is passed into an alkaline earth hydroxide, at first the carbonate is precipitated; but later, as the concentrations of H^+ and HCO_3^- increase, the precipitate will dissolve.

Hydroxides.—The hydroxides of Group IV are moderately soluble. High concentrations of OH^- ions, as in NaOH and KOH solutions, give white precipitates with Ba^{++} , Sr^{++} , and Ca^{++} . NH_4OH is too weak a base to furnish the requisite OH^- concentration.

Chromates.—The cations of the alkaline earths combine with CrO_4^{--} , forming yellow chromates. They are soluble in strong acids, owing to the removal of the CrO_4^{--} ion by the H^+ ion as $\text{Cr}_2\text{O}_7^{--}$ (or, more probably, HCrO_4^-).

The greatest difference in solubilities in Group IV is found in the chromates (see Table 33). BaCrO_4 is so insoluble in water that a very small CrO_4^{--} concentration is sufficient for its precipitation. SrCrO_4 , on the other hand, is precipitated by a somewhat higher concentration. The problem is to keep the CrO_4^{--} concentration low enough not to exceed the solubility product of SrCrO_4 at any time. Very dilute K_2CrO_4 is not a practical reagent, for several hundred cubic centimeters might be necessary to precipitate all the Ba^{++} in the solution. A much cleverer procedure is to use a solution that maintains a definite, though low, concentration of CrO_4^{--} . This is found in $\text{K}_2\text{Cr}_2\text{O}_7$ in a solution of constant acidity. This constant acidity may be

realized in a solution of $\text{HC}_2\text{H}_3\text{O}_2$, buffered by an excess of $\text{C}_2\text{H}_3\text{O}_2^-$ ions. The whole equilibrium may be represented thus:



In solutions containing very large concentrations of Sr^{++} , some SrCrO_4 may be precipitated along with the BaCrO_4 , but most of the Sr^{++} will remain in solution. The BaCrO_4 may be separated from this excess SrCrO_4 by dissolving the precipitate in the smallest amount of dilute HNO_3 and adding an excess of $\text{NaC}_2\text{H}_3\text{O}_2$ solution. The concentrations of Sr^{++} and CrO_4^{--} in this second solution are now too small to exceed the solubility product of SrCrO_4 , and only BaCrO_4 can form. The inference is that, whenever large amounts of Sr^{++} are found, the BaCrO_4 precipitate should be dissolved and reprecipitated, to be sure that it is not SrCrO_4 .

It should be noted that the presence of $\text{C}_2\text{H}_3\text{O}_2^-$ affects the solubilities of SrCrO_4 and BaCrO_4 in the same direction. It reduces both of them. The $\text{C}_2\text{H}_3\text{O}_2^-$ does not act as a wedge to increase the difference in solubilities.

Sulfates.—The SO_4^{--} ion precipitates Ba^{++} , Sr^{++} , and Ca^{++} as white precipitates. Again, considerable differences in solubility are found, though not so great as with the chromates. The sulfates differ from the chromates in not being appreciably soluble in HCl and HNO_3 . This is owing to the fact that the H^+ ion exercises little shift on the ionic equilibria. The possible products are HSO_4^- and H_2SO_4 , which are strong electrolytes and therefore practically completely ionized. The sulfates are considerably soluble in concentrated H_2SO_4 , which converts the SO_4^{--} ion into HSO_4^- , and the hydrogen sulfates of the alkaline earths are soluble.

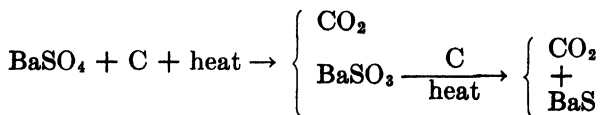
The differences in solubility of BaSO_4 , SrSO_4 , and CaSO_4 make possible a certain degree of selective precipitation. BaSO_4 tends to precipitate before SrSO_4 , and SrSO_4 before CaSO_4 . However,

the differences in solubility are not great enough to permit of an even approximate separation. On the other hand, Ba^{++} solutions give a precipitate of BaSO_4 with saturated CaSO_4 and saturated SrSO_4 , and Sr^{++} solutions give a precipitate of SrSO_4 with saturated CaSO_4 . By these reactions, Ba^{++} may be tested for in the presence of Sr^{++} or Ca^{++} , and Sr^{++} in the presence of Ca^{++} , but not Sr^{++} in the presence of Ba^{++} .

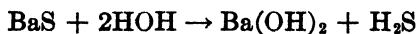
It is to be expected that a precipitate of CaSO_4 should form when a solution of a soluble Ca^{++} salt is added to saturated CaSO_4 . The common-ion effect calls for a repression of solubility. No precipitate appears—at least, not an immediate precipitate. It should be remembered that CaSO_4 solution is diluted considerably by the added solution. But probably more important is the salt effect (page 194). Perhaps supersaturation also plays a part.

Strontium sulfate is notorious for its slow precipitation from solutions. In dilute solutions, 10 to 15 min. may elapse before a precipitate appears; and complete precipitation may take hours. This slow precipitation is hard to explain. One theory is that Sr^{++} and SO_4^{--} ions are present in solution in highly hydrated forms, so that the molecules as first formed are also highly hydrated and therefore very soluble. The dehydration of these solvated molecules is the slow step in the reaction.

Sulfides.—When alkaline earth sulfates are heated with carbon, they are reduced first to sulfites and then to sulfides; *e.g.*,



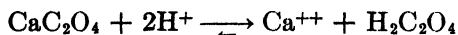
Sulfides formed in this way are fairly soluble in water but decompose upon standing; *e.g.*,



The H_2S may be tested for by appropriate reactions. This is an important method for bringing these insoluble sulfates into solution.

Oxalates.—The $\text{C}_2\text{O}_4^{--}$ ion precipitates the alkaline earth cations as white precipitates. Calcium oxalate is the most insoluble, being practically insoluble in $\text{HC}_2\text{H}_3\text{O}_2$. All are easily

soluble in HCl and HNO₃. This is owing to the fairly low ionization of oxalic acid; *e.g.*,



Fluorides.—The fluorides of the alkaline earths are white and insoluble in water. BaF₂ and SrF₂ are more soluble than CaF₂, and dissolve fairly well in strong acids, solutions of certain salts, etc. CaF₂ is difficultly soluble in strong acids. An evidence of its high insolubility is that it precipitates in a gelatinous form.

Phosphates.—Neutral phosphate solutions contain the HPO₄[—] anion. A certain degree of alkalinity is necessary to convert this ion into the PO₄[—] ion: $\text{HPO}_4^{—} + \text{OH}^- \rightleftharpoons \text{PO}_4^{—} + \text{H}_2\text{O}$. Consequently the alkaline earth ions in neutral solution form secondary phosphates (*e.g.*, CaHPO₄) and in alkaline solutions form tertiary phosphates [*e.g.*, Ca₃(PO₄)₂]. All the phosphates are white precipitates, readily soluble in HCl or HNO₃.

Ferrocyanides.—The ferrocyanide ion Fe(CN)₆[—] forms soluble salts with Ba⁺⁺ and Sr⁺⁺, but with Ca⁺⁺ it forms insoluble salts of various compositions. The most insoluble of these is CaK₂Fe(CN)₆·4Ca(NH₄)₂Fe(CN)₆, formed when a Ca⁺⁺ solution is treated with an excess of NH₄Cl and K₄Fe(CN)₆ solutions. For the sake of simplicity, the formula is written CaNH₄KFe(CN)₆, and its formation represented:



This “triple ferrocyanide” tends to be sparingly soluble, and excess of NH₄⁺, K⁺, and Fe(CN)₆[—] ions are used to reduce this solubility by the common-ion effect. This precipitate is creamy white in color and is decomposed by strong acids.

Acidified solutions of K₄Fe(CN)₆ are not stable and upon standing or heating turn blue, and a bluish precipitate, resembling Prussian blue, forms. Consequently, the reagents must not be added to a hot solution, and a precipitate should form promptly when Ca⁺⁺ is present.

Flame Reactions.—Volatile compounds of the alkaline earths give the following characteristic colors to the Bunsen flame: Ba⁺⁺, green; Sr⁺⁺, crimson; and Ca⁺⁺, red. The chlorides, on account of their volatility, are usually employed. Many non-volatile compounds—*e.g.*, the oxides, oxalates, etc.—may be

made to give flame reactions by dipping the platinum wire carrying the nonvolatile material in concentrated HCl. Other compounds, such as the sulfates, give at best only feeble tests.

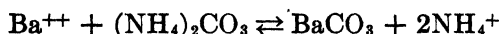
These tests are not sufficiently reliable for positive identifications, owing to numerous interferences. A small amount of Ca^{++} or Na^+ compound will mask a large amount of Ba^{++} , and it is impossible to distinguish a strong Ca^{++} flame from a weak Sr^{++} flame. These tests should be used as confirmatory, only.

Confirmatory Tests.—Outside of the flame reactions, the ions of Group IV have no highly specific tests. The nearest approach is the precipitation of sulfates by saturated solutions of slightly more soluble sulfates. The reactions used in separating the ions are sufficiently definite to obviate the need of confirmatory tests.

ANALYTICAL PROCEDURES

Interferences in the Filtrate from Group III.—The filtrate from Group III probably contains S^{--} and S_x^{--} ions, and perhaps NiS. These must be removed, for otherwise they may create a false impression that Group IV ions may be present. The solution is acidified with $\text{HC}_2\text{H}_3\text{O}_2$ and boiled as long as the vapors contain H_2S . Any precipitate of S, NiS, etc., is filtered out and rejected.

Solubility of Carbonates in Ammonium Salt Solutions.—The precipitation of the alkaline earth carbonates is never complete, owing to a reversibility in the reaction; *e.g.*,



The leftward tendency in this equation seems to be due to the low ionization of $(\text{NH}_4)_2\text{CO}_3$. In spite of its salt nature, $(\text{NH}_4)_2\text{CO}_3$ is a weak electrolyte. There are several considerations that support this inference: (1) Its solution is a poor conductor of the electric current. (2) Its slow reactions suggest a low concentration of CO_3^{--} ions. (3) The shift in equilibrium when NH_4^+ ions are added to suspensions of alkaline earth carbonates is most readily explained by the formation of stable complexes or molecules. This low ionization is partly due to hydrolysis into weak base and weak acid: $(\text{NH}_4)_2\text{CO}_3 + \text{HOH} \rightleftharpoons \text{NH}_4^+ + \text{NH}_4\text{OH} + \text{HCO}_3^-$.

The extent of this solvent action of NH_4^+ ions on the carbonates of Group IV is greater than might be expected. The

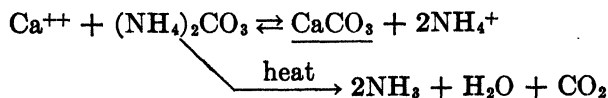
solubility of BaCO_3 in varying concentrations of NH_4Cl at 30° is shown below. Attention is called to the magnitude of this effect.

Concentration of NH_4Cl , moles per liter	Concentration of Ba^{++} , millimoles per liter	Milligrams of Ba^{++} in 100 cc. of solution
0	0.18	2.5
1	6.2	85
2	8.5	117
3	10.0	137
4	11.0	151
5	11.5	158

Evidently, excessive amounts of NH_4^+ interfere seriously with the analysis of Group IV. Small amounts of Ba^{++} , Sr^{++} , and Ca^{++} may be missed altogether, to be precipitated later in Group V as insoluble phosphates, giving a false indication of the presence of Mg^{++} ions. Care should be taken in Group III not to add unnecessary amounts of NH_4OH and NH_4Cl .

Large excesses of NH_4^+ may normally be present in some cases; *e.g.*, the original substance may contain considerable NH_4^+ , or the Group IV solution may be a filtrate from a basic acetate separation. In such cases, the whole of the NH_4^+ should be removed by adding HNO_3 , evaporating, and igniting (see page 305). After solution of the residue, NH_4OH is slowly added; and, if a turbidity appears [due to $\text{Mg}(\text{OH})_2$], enough NH_4Cl is added to clear the solution.

Solvent Action of Boiling NH_4^+ Solutions.—If the carbonates of Group IV are boiled in their mother liquor, they will go back into solution. The equilibrium in the precipitation reaction is completely displaced to the left by the decomposition of the $(\text{NH}_4)_2\text{CO}_3$ into gaseous NH_3 and gaseous CO_2 .



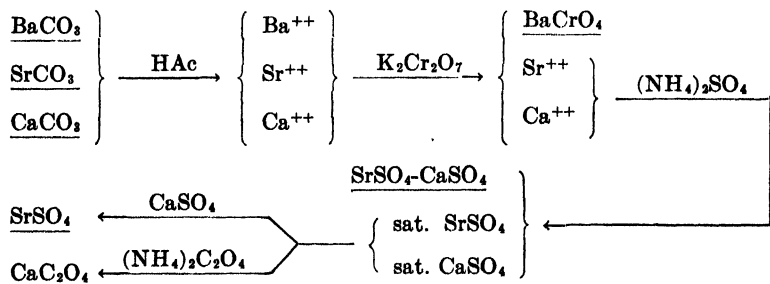
For this reason, the burner is withdrawn from beneath the solution just after the addition of the $(\text{NH}_4)_2\text{CO}_3$.

Precipitation from Hot, Concentrated Solution.—Before precipitating Group IV, the solution is concentrated to a volume of about 25 cc. and heated to boiling. A small excess of $(\text{NH}_4)_2\text{CO}_3$ is added, and the hot mixture allowed to stand, without further heating, about 15 min. This hot precipitation has the following advantages: (1) The precipitate is more crystalline and filters better. (2) Any hydrogen carbonates [*e.g.*, $\text{Ca}(\text{HCO}_3)_2$] are decomposed. (3) Any ammonium carbamate, NH_4CONH_2 , in the reagent is converted into $(\text{NH}_4)_2\text{CO}_3$.

There are several procedures for the analysis of this group, of which the following are the most important.

The Chromate-Sulfate-Oxalate Procedure.—Important points in this procedure are: (1) Ba^{++} is separated as BaCrO_4 in the presence of buffered $\text{HC}_2\text{H}_3\text{O}_2$. (2) After the filtrate is tested for Sr^{++} , excess of SO_4^{--} is added, precipitating most of the Sr^{++} and Ca^{++} as sulfates and leaving a saturated solution of SrSO_4 and CaSO_4 . (3) This saturated solution, when treated with $\text{C}_2\text{O}_4^{--}$, precipitates CaC_2O_4 only. The procedure is diagrammed in Table 34.

TABLE 34.—THE CHROMATE-SULFATE-OXALATE METHOD



1. In solutions containing high concentrations of Sr^{++} , some SrCrO_4 may be precipitated along with the BaCrO_4 . For this reason, whenever the test for Sr^{++} is strong, the supposed BaCrO_4 precipitate may contain SrCrO_4 only. In this case, it should be dissolved in dilute HNO_3 and the solution evaporated almost to dryness to expel excess of HNO_3 . The residue is taken up in water, and $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ is added. A second precipitate can be BaCrO_4 only.

2. The $\text{C}_2\text{O}_4^{--}$ ion precipitates CaC_2O_4 only from saturated $\text{SrSO}_4\text{-CaSO}_4$ solution. SrC_2O_4 has about the same solubility as SrSO_4 , and no precipitation of Sr^{++} is to be expected. CaSO_4 , on the contrary, is about two hundred

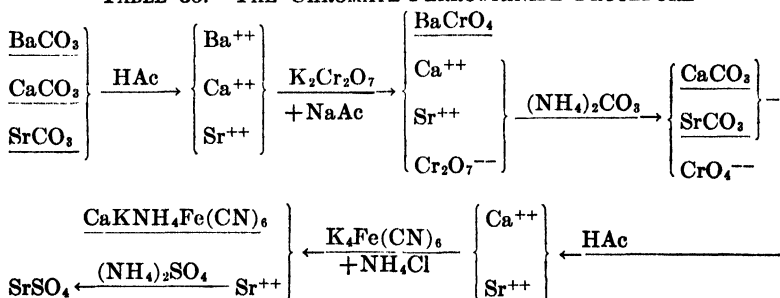
fifty times as soluble as CaC_2O_4 , and the solubility product of the latter is easily exceeded.

3. In the presence of Sr^{++} , false tests for Ca^{++} are frequently obtained. Examination shows that the precipitates are SrSO_4 , owing to incomplete precipitation of SrSO_4 before the test is made for Ca^{++} .

4. In the presence of Sr^{++} , a doubtful test for Ca^{++} should be confirmed by adding a little H_2SO_4 and warming. If a precipitate still remains, filter, make the filtrate alkaline with NH_4OH , and add a little $(\text{NH}_4)_2\text{C}_2\text{O}_4$. The final precipitate is CaC_2O_4 .

The Chromate-Ferrocyanide Procedure.—In this procedure, (1) Ba^{++} is precipitated as BaCrO_4 , (2) Ca^{++} is precipitated as the triple ferrocyanide, and (3) Sr^{++} is precipitated as SrSO_4 . The procedure is outlined in Table 35.

TABLE 35.—THE CHROMATE-FERROCYANIDE PROCEDURE

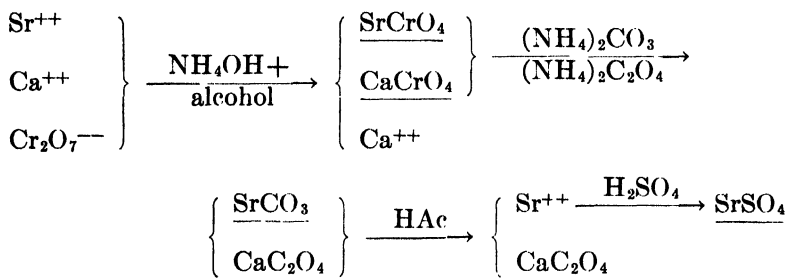


1. The excess of $\text{Cr}_2\text{O}_7^{--}$ must be removed before adding $\text{K}_4\text{Fe}(\text{CN})_6$, for these reagents react with each other, forming a blue precipitate—possibly Prussian blue. It is easier to precipitate Sr^{++} and Ca^{++} than $\text{Cr}_2\text{O}_7^{--}$. So these cations are thrown down as SrCO_3 and CaCO_3 , and the filtrate containing the CrO_4^{--} ions is discarded.

2. The triple ferrocyanide precipitation must be made on *cold* solutions, to avoid a bluish precipitate caused by the decomposition of acidified ferrocyanides.

3. The test for Ca^{++} is made more sensitive by increasing the concentrations of the ions involved. The concentration of the Ca^{++} can be increased only by boiling the solution to be tested down to a small volume. The concentrations of the K^+ and $\text{Fe}(\text{CN})_6^{--}$ can be increased by using an excess of $\text{K}_4\text{Fe}(\text{CN})_6$, and the NH_4^+ by using an excess of NH_4Cl . An excess of $\text{K}_4\text{Fe}(\text{CN})_6$ is more effective than a corresponding amount of NH_4Cl , since every molecule of the ferrocyanide introduces four K^+ ions and one $\text{Fe}(\text{CN})_6^{--}$ ion, while a molecule of the ammonium salt introduces only one NH_4^+ ion—approximately a 5-to-1 advantage.

Separation of Sr^{++} as SrSO_4 .—In the A. A. Noyes procedure for Group IV, Sr^{++} is separated as SrCrO_4 by adding NH_4OH to the filtrate from the BaCrO_4 precipitate. The steps are outlined as follows:



1. The NH_4OH converts $\text{Cr}_2\text{O}_7^{--}$ into CrO_4^{--} ions: $\text{Cr}_2\text{O}_7^{--} + 2\text{NH}_4\text{OH} \rightarrow 2\text{CrO}_4^{--} + 2\text{NH}_4^+$. This increase in the concentration of the CrO_4^{--} ions causes the solubility product of SrCrO_4 to be exceeded, so that precipitation takes place.

2. Since the solubility of SrCrO_4 is 0.006 mole per liter, the precipitation is far from complete. Alcohol is therefore added, to reduce this solubility to analytical requirements.

3. Strontium chromate precipitated in the presence of alcohol is finely divided and tends to "run through the filter." Filter-paper pulp is added to adsorb the precipitate and to improve filtration.

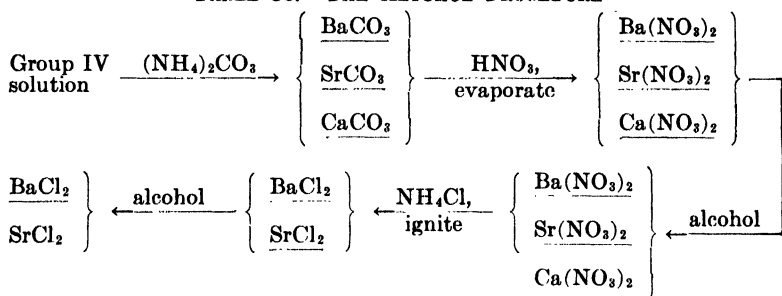
4. A small amount of CaCrO_4 is always "carried down" in the SrCrO_4 precipitate. Small amounts of $(\text{NH}_4)_2\text{CO}_3$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ are added, transposing the chromates into SrCO_3 and CaC_2O_4 . It should be noted that Sr^{++} and Ca^{++} each combine with the anion forming the most insoluble precipitate. After washing, the precipitate is treated with $\text{HC}_2\text{H}_3\text{O}_2$, which dissolves the SrCO_3 but not the CaC_2O_4 . The Sr^{++} may then be detected by precipitation with SO_4^{--} .

Alcoholic Procedure.—It is an interesting fact that, as a rule, deliquescent substances are soluble in alcohol, while nondeliquescent substances are insoluble. One of the most noteworthy exceptions to the rule is HgCl_2 , soluble in alcohol and yet not deliquescent. This rule seems to have no theoretical basis other than that substances that readily form hydrates with water may be expected to form solvates with solvents similar to water. This rule is illustrated in the alcoholic procedure below.

The carbonates are precipitated as usual and then converted into nitrates by adding HNO_3 and evaporating to dryness. (1) $\text{Ca}(\text{NO}_3)_2$ is deliquescent, whereas $\text{Ba}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2$ are not. Hence $\text{Ca}(\text{NO}_3)_2$ may be extracted

from the other nitrates by means of alcohol. (2) Next, $\text{Ba}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2$ are converted into BaCl_2 and SrCl_2 by igniting with NH_4Cl . (3) The deliquescent SrCl_2 is then extracted by alcohol, leaving BaCl_2 in the residue. The procedure is outlined in Table 36.

TABLE 36.—THE ALCOHOL PROCEDURE



Careful examination of this procedure shows that it is not quantitative.

Inclusion of Mg^{++} in Group IV.—In the presence of alcohol, $(\text{NH}_4)_2\text{CO}_3$ precipitates Mg^{++} as $\text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$. A modification of the usual procedure, based on this fact, involves including Mg^{++} in Group IV by carrying out the group precipitation in 50 per cent alcoholic solution. Since Mg^{++} is not precipitated by any of the reagents for Ba^{++} , Sr^{++} , or Ca^{++} , it may be detected in the filtrate after their removal by precipitation as MgNH_4PO_4 .

Exercises

1. Judging from their position in the Periodic Table, would you expect the alkaline earth ions to form NH_3 complexes?
2. Explain why traces of Group IV ions are normally carried into Group V.
3. What effect does the addition of $\text{NaC}_2\text{H}_3\text{O}_2$ have on the composition of $\text{K}_2\text{Cr}_2\text{O}_7$ solution? Explain your answer.
4. What error would occur if, in the test for Ca^{++} by NH_4Cl and $\text{K}_4\text{Fe}(\text{CN})_6$, the solution is warmed or allowed to stand?
5. Why does $\text{Cr}_2\text{O}_7^{--}$ precipitate Sr^{++} in alkaline, but not in acid, solution?
6. Why are Ca^{++} and Sr^{++} reprecipitated as carbonates and then redissolved after the removal of Ba^{++} as BaCrO_4 ?
7. CaSO_4 is more soluble in water than CaC_2O_4 . Explain why CaC_2O_4 is more soluble in HCl than CaSO_4 .
8. Identify the following cations of Group IV: (a) A cation that gives a precipitate with saturated CaSO_4 , but none with saturated SrSO_4 . (b) A

cation that gives no precipitate with $K_2Cr_2O_7$ in either acid or alkaline solution. (c) A cation that gives a precipitate with $(NH_4)_2CO_3$, but none with $K_2Cr_2O_7$ in the presence of $HC_2H_3O_2$, and none with $K_4Fe(CN)_6 + NH_4Cl$. (d) A cation that gives precipitates with K_2CrO_4 and $(NH_4)_2C_2O_4$, both soluble in $HC_2H_3O_2$.

9. Give reagents and products in the following separations: (a) Ba^{++} and Ca^{++} ; (b) Mg^{++} and Ca^{++} ; (c) Ba^{++} and Pb^{++} ; (d) Sr^{++} and Ca^{++} .

CHAPTER XVIII

GROUP V—THE SOLUBLE GROUP

This group consists of the following members:

Magnesium, Mg^{++}	[Lithium, Li^+]
Ammonium, NH_4^+	[Cesium, Cs^+]
Potassium, K^+	[Rubidium, Rb^+]
Sodium, Na^+	

The elements cesium and rubidium are rare, and the expensive-ness of their compounds excludes them from consideration in elementary courses in qualitative analysis.

This group is called the *soluble group*, since it forms few insoluble compounds and none of them have a high insolubility. There is no group reagent that will precipitate the group as a whole.

One way of defining the group is to say that it consists of those cations which have not been precipitated in preceding groups. This statement may be taken to imply that they are a group of "leftovers"; or, using the vernacular of the bargain counter, they are an assortment of "remnants" and "misfits" grouped together without regard to kind or class. This is true to a certain extent; Mg^{++} does not resemble the other members very closely. NH_4^+ , K^+ , and Na^+ , on the other hand, form as definite a group as Ni^{++} , Co^{++} and Fe^{++} , or Ca^{++} , Sr^{++} , and Ba^{++} . The remnant-counter figure of speech, however, is still apropos in another respect, *viz.*: they are badly shopworn. They carry with them all the detritus of previous operations, frequently including appreciable amounts of Al^{+++} , Ca^{++} , Sr^{++} , and Ba^{++} , incompletely precipitated in preceding groups.

Removal of Traces of Group IV Ions.—Owing to a certain solubility of the carbonates of Ba^{++} , Sr^{++} , and Ca^{++} in NH_4^+ solution (see page 292), appreciable amounts of these ions are carried into Group V. Al^{+++} may also be present, if the Group III and Group IV solutions were too alkaline with NH_4OH . These foreign ions must be removed as completely as possible, for

they form insoluble phosphates and in this way interfere with the test for Mg^{++} . BaSiF_6 is also quite insoluble, so that the presence of Ba^{++} would give a false test for Na^+ . To remove these interferences, small amounts of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solutions are added to the filtrate from Group IV. The mixture is allowed to stand for about 15 min., and any precipitate is noted and removed by filtration.

The function of the $(\text{NH}_4)_2\text{SO}_4$ is to remove Ba^{++} and Sr^{++} as BaSO_4 and SrSO_4 , and that of the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ is to remove the Ca^{++} as CaC_2O_4 . In case any one of these ions has not been found in Group IV, the effect of these reagents should be closely observed. Otherwise, small amounts of the Group IV cations may escape detection.

MAGNESIUM

The Metal.—Magnesium is a very active metal. Its stability at ordinary temperatures is due to a protective coating of the oxide, MgO . It dissolves in acids, almost with violence, forming solutions containing the divalent cation Mg^{++} .

Magnesium is used in light alloys (with aluminum), in flashlight powders, and as a deoxidizer in alloys and a "getter" in radio tubes. Its salts are extensively used in medicine and the industries.

The Ion.—Magnesium forms a single cation Mg^{++} . This ion resembles several other cations in a desultory fashion. Its position in the Periodic Table indicates that it should resemble the ions of Group IV. Really, its most conspicuous difference from Ca^{++} , Sr^{++} , and Ba^{++} is the ready solubility of MgCO_3 in NH_4^+ salt solutions. It resembles Zn^{++} and Cd^{++} in many respects but differs in that the sulfide is decomposed by water. It also resembles Mn^{++} but differs in its nonoxidizability to higher valences and the instability of its sulfide. Manganese dioxide was once called *black oxide of magnesia*.

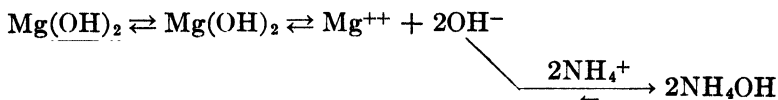
Solubilities.—Among the commoner soluble salts of Mg^{++} are to be listed MgCl_2 , MgSO_4 , $\text{Mg}(\text{NO}_3)_2$, etc. The important insoluble compounds are MgO , $\text{Mg}(\text{OH})_2$, MgCO_3 [or $\text{Mg}(\text{OH})_2 \cdot \text{MgCO}_3$], MgNH_4PO_4 , etc.

Magnesium Hydroxide.— $\text{Mg}(\text{OH})_2$ is a white, gelatinous precipitate, formed when a base is added to a solution of Mg^{++} ions. It is easily soluble in acids, soluble in NH_4^+ salt solutions,

but insoluble in strong bases. It differs from $\text{Zn}(\text{OH})_2$ in having no acid properties. Upon ignition, it forms the oxide, thus: $\text{Mg}(\text{OH})_2 + \text{heat} \rightarrow \text{MgO} + \text{H}_2\text{O}$.

$\text{Mg}(\text{OH})_2$ is fairly insoluble in water—about 0.0002 mole per liter at ordinary temperatures. The expression for its solubility product is as follows: $[\text{Mg}^{++}] \times [\text{OH}^-]^2 = 0.0002 \times 0.0004^2 = 3.2 \times 10^{-11}$.

The solubility of $\text{Mg}(\text{OH})_2$ in NH_4^+ solutions is explained by most authorities as due to the repression of the OH^- ion by the excess NH_4^+ . That is, the concentration of the OH^- ion is reduced to such a small value that the solubility product of $\text{Mg}(\text{OH})_2$ is not exceeded. The equilibria are represented thus:

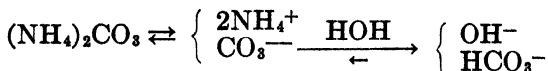


Though $\text{Mg}(\text{OH})_2$ is fairly insoluble in water, its solubility in NH_4^+ solutions and its colloidal nature make it unsuited for ordinary separations.

Magnesium Carbonate.—When an alkali carbonate, such as Na_2CO_3 , is added to a Mg^{++} solution, a white precipitate of the basic carbonate is formed. The formula is $\text{Mg}(\text{OH})_2 \cdot \text{MgCO}_3$. The normal carbonate, MgCO_3 , is found in nature.

The solubility of MgCO_3 is 5.1×10^{-3} mole per liter, giving a solubility product of 2.6×10^{-5} . It should be noticed that the carbonate is more soluble than the hydroxide. As a result, MgCO_3 tends to hydrolyze into $\text{Mg}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2 \cdot \text{MgCO}_3$.

Like the hydroxide, magnesium carbonates are readily soluble in NH_4^+ solutions. The failure of MgCO_3 to precipitate when $(\text{NH}_4)_2\text{CO}_3$ is added to Mg^{++} solutions must be attributed to low concentrations of Mg^{++} or CO_3^{--} ions, or of both. $(\text{NH}_4)_2\text{CO}_3$ is not a strong electrolyte, and probably the principal anion products are OH^- and HCO_3^- .



Since $\text{Mg}(\text{HCO}_3)_2$ is soluble in water, the probable precipitate

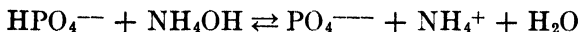
should be $\text{Mg}(\text{OH})_2$. But, as seen on page 300, $\text{Mg}(\text{OH})_2$ is soluble in NH_4^+ solutions.

Another possible explanation is that Mg^{++} forms with NH_4^+ the complex ion $\text{Mg}(\text{NH}_4)_2^{++++}$. The principal evidence in support of this theory is that $\text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ may be precipitated by the addition of alcohol.

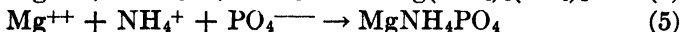
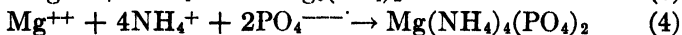
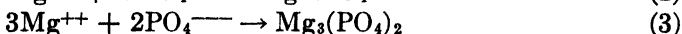
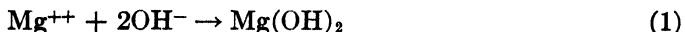
Magnesium Ammonium Phosphate.— Mg^{++} is almost always precipitated in the form MgNH_4PO_4 , for this compound is crystalline and filters well.



The reagents used in this precipitation are NH_4OH , NH_4Cl , and Na_2HPO_4 . The role of the NH_4OH is to convert HPO_4^{--} ions into PO_4^{---} ions.



The NH_4Cl is used to repress the ionization of the NH_4OH , so that the concentration of the OH^- ions will not be too large. There are therefore present in the mixture the following ions: Mg^{++} , NH_4^+ , OH^- , HPO_4^{--} , and PO_4^{---} . The following precipitations are possible with this set of ions:



Equation (1) will take place when the OH^- concentration is too high. It may be prevented by introducing a certain amount of NH_4^+ ions— NH_4Cl , for example. Equation (2) will occur when the solution is not sufficiently alkaline, *i.e.*, when not enough NH_4OH is present to convert HPO_4^{--} into PO_4^{---} . Equation (3) will occur when the solution is too alkaline, giving a concentration of PO_4^{---} large enough to exceed the solubility product of $\text{Mg}_3(\text{PO}_4)_2$. Equation (4) will occur in strongly alkaline solutions, containing a large excess of NH_4^+ ions.

It is important to precipitate Mg^{++} in the right form, not only to make the precipitation as complete as possible, but also to make it as distinctive as possible. $\text{Mg}(\text{OH})_2$, MgHPO_4 , and

$\text{Mg}_3(\text{PO}_4)_2$ are colloidal and resemble $\text{Al}(\text{OH})_3$ and CaHPO_4 —possible interfering substances. This calls for a careful regulation of ion concentrations so that conditions will be favorable to the formation of MgNH_4PO_4 only. These equations indicate that there should be (a) a slight, but definite alkalinity, (b) no large excess of NH_4^+ ions, and (c) high concentrations of the Mg^{++} and HPO_4^{--} ions. These conditions are realized in the following procedure.

Precipitation of MgNH_4PO_4 .—The solution is evaporated to a small volume—say 10 cc.—and thoroughly cooled. Any precipitate of NH_4^+ salts that may form is filtered out. The solution is then strongly acidified with HCl or HNO_3 , and about 5 cc. of 0.25 *M* Na_2HPO_4 added. This Na_2HPO_4 solution should be filtered to remove any dregs of CaHPO_4 and $\text{Si}(\text{OH})_4$ formed by its attack on the glass of the reagent bottles. The clear solution is then heated to boiling, and a slight excess of concentrated NH_4OH is slowly added, with shaking. The mixture is then allowed to stand until it is cold. The precipitate that first separates may be amorphous (possibly MgHPO_4), but on cooling it changes over into MgNH_4PO_4 .

Precipitation of Magnesium Quinolate.— Mg^{++} ions are precipitated by “8-hydroxyquinoline,” $\text{C}_9\text{H}_6\text{NOH}$, as magnesium quinolate, $\text{Mg}(\text{C}_9\text{H}_6\text{NO})_2$, in dilute NH_3 solution. This gives a separation of Mg^{++} from Li^+ . Li^+ and Mg^{++} are both precipitated as phosphates and therefore interfere with the detection of each other.

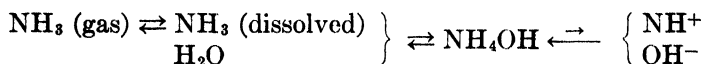
Lake Formation.—Two Japanese chemists, Suitzu and Okuma, discovered in 1926 that the dye para-nitrobenzene-azo-resorcinol forms a blue precipitate with Mg^{++} in slightly alkaline solution. Co^{++} and Ni^{++} interfere by also forming precipitates.

Detection.— Mg^{++} ions are usually separated as MgNH_4PO_4 . This precipitate may be contaminated by AlPO_4 , CaHPO_4 , etc., unless the preceding separations have been carried out carefully. In the presence of Li^+ , the Mg^{++} is thrown down as the quinolate. In either case, the presence of Mg^{++} should be confirmed by the lake test with *p*-nitrobenzene-azo-resorcinol.

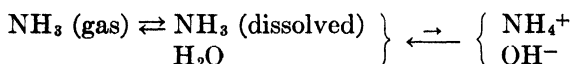
Ammonium, NH_4^+

The ion NH_4^+ , corresponding to the hypothetical metal ammonium, resembles K^+ and Na^+ in its chemical behavior— K^+ more closely than Na^+ .

The Base Ammonia (Ammonium Hydroxide).—The gas ammonia is very soluble in water, giving a basic solution whose composition is usually represented as follows:



There are some who consider NH_4OH completely ionized and therefore nonexistent. They express the equilibrium thus:



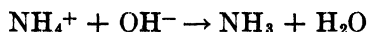
NH_3 may be thought of as a base in itself, combining directly with the H^+ ion, without any mediation of hydroxide: $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$. This concept is most suitable for explaining the dissociation of NH_4^+ salts by heat.

Ammonia solution (or ammonium hydroxide) is a weak base. Its electrical conductivity indicates that its molar solution is only 0.4 per cent ionized. Its ionization constant is therefore 1.7×10^{-5} . The above equilibria are displaced to the left by heat, and the NH_3 may be completely expelled by boiling.

Solubilities.—All NH_4^+ salts are soluble except the cobaltinitrite, $(\text{NH}_4)_2\text{NaCo}(\text{NO}_2)_6$, the hydrogen tartrate, $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$, the chloroplatinate, $(\text{NH}_4)_2\text{PtCl}_6$, and a few others. Note that these solubilities parallel those of the K^+ salts. NH_4^+ differs from K^+ in the moderate solubility of the perchlorate, NH_4ClO_4 , and the fluosilicate, $(\text{NH}_4)_2\text{SiF}_6$.

Reactions.—The following are the most important of the analytical reactions of NH_4^+ and NH_3 .

Displacement by Strong Bases.— NH_4^+ salts are decomposed by strong bases, giving NH_3 gas.

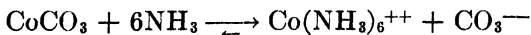
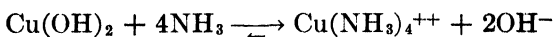
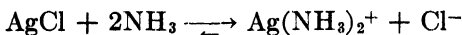


Precipitation.— NH_4^+ gives precipitates with the following reagents: with $\text{Na}_2\text{Co}(\text{NO}_2)_6$, $(\text{NH}_4)_2\text{NaCo}(\text{NO}_2)_6$, yellow, resembling the corresponding K^+ salt; with $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ in $\text{HC}_2\text{H}_3\text{O}_2$ solution, $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$, white, soluble in acids and bases; with high concentrations of ClO_4^- or NH_4^+ , NH_4ClO_4 may form, moderately soluble in water. In acid solutions, NH_4^+ gives no precipitate with SiF_6^- ; but in alkaline solution, and sometimes

in neutral solution, $(\text{NH}_4)_2\text{SiF}_6$ is hydrolyzed, forming white $\text{Si}(\text{OH})_4$.



Complex Formation.— NH_3 forms complex cations with the following: Ag^+ , Cu^{++} , Cu_2^{++} , Cd^{++} , Zn^{++} , Fe^{++} , Ni^{++} , Co^{++} , Cr^{+++} , and possibly a few others, such as Mn^{++} and Mg^{++} . These complex ions vary in stability, but as a rule they are very stable. As a result, many of the precipitates of this list of cations dissolve in NH_3 solution; *e.g.*,



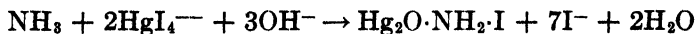
In these complex cations, the number of NH_3 molecules is twice the highest valence of the cation. This rule breaks down in the case of the H^+ ion, which combines with *one* NH_3 to form $\text{H}(\text{NH}_3)^+$ or NH_4^+ . Ni^{++} and Co^{++} also form complexes with a variable NH_3 content; Co^{++} forms complexes containing any number from one to six. Most of these complex cations are broken down by H_2S , owing to the greater stability (*i.e.*, insolubility) of the sulfides.

NH_3 reacts with Hg^{++} compounds, forming mercury-amino compounds (see page 189) which do not show the usual properties of NH_4^+ ; *e.g.*,



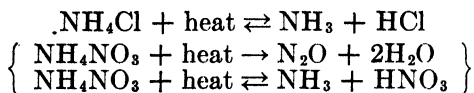
This compound does not evolve NH_3 when warmed with NaOH .

With a KOH solution containing HgI_4^{--} (see page 190), NH_3 forms the very insoluble brown $\text{Hg}_2\text{O} \cdot \text{NH}_2 \cdot \text{I}$, which is the basis of the very delicate Nessler test for NH_3 (see following paragraphs).



Removal.— NH_4^+ may interfere with the tests for K^+ and Na^+ , particularly if NH_4^+ is present in quantity. So it is better to remove NH_4^+ completely before starting on the tests for K^+ and

Na^+ . This is done by evaporating the solution to dryness and igniting the mixture either as chlorides or as nitrates.



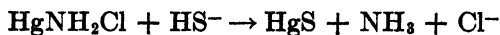
As represented in the second and third equations, NH_4NO_3 decomposes simultaneously in two ways—mainly according to the first. It should be noticed that the first and the third reactions are reversible, while the second is irreversible. In the reversible reactions, the salts tend to re-form on the walls of the beaker, so that careful heating of the walls is necessary for the complete expulsion of the NH_4^+ . Ignition as nitrates is preferable for several reasons: (1) It proceeds at a lower temperature, (2) it has less tendency toward reversibility, and (3) the oxidizing action of the HNO_3 removes organic impurities introduced in ammonium compounds, filter paper, etc.

NH_4^+ salts could be removed by ignition as sulfates, but the temperature required would be much higher than with chlorides and nitrates.

Detection.—The test for NH_4^+ must be made on a portion of the original, for NH_4^+ has been introduced into the solution during the analysis of Groups III and IV. The following are the tests used.

1. *Evolution-of- NH_3 Method.*—If NH_4^+ ions may be present in ordinary amounts, the substance is warmed with NaOH solution. The NH_3 evolved may be recognized by (a) its odor, or (b) its bluing of red litmus paper. In the litmus test, the mixture must not be allowed to boil, for enough NaOH may be carried up in the spray to cause a blue color.

Hg^{++} salts interfere with this test by forming nonvolatile amino complexes (see page 189). This interference may be obviated by using Na_2S along with the NaOH . For example,



2. *The Nessler Test.*—In cases where the NH_4^+ ion is present as a trace only—e.g., in drinking waters¹—the Nessler test is

¹ The ammonia in surface water is due to pollution (sewage, frequently) which contains organic matter that undergoes slow decomposition, forming, among other things, NH_3 .

used. A sample of the water is made alkaline with Na_2CO_3 or NaOH and distilled. The NH_4^+ will pass into the distillate as NH_3 . The Nessler reagent, consisting of a solution of K_2HgI_4 and KOH , is then added. If appreciable amounts of NH_3 are present, a brown precipitate of $\text{Hg}_2\text{O} \cdot \text{NH}_2 \cdot \text{I}$ is formed; if only a trace of NH_3 is present, only a yellow coloration is visible. Many cations would interfere with this test by forming precipitates with the OH^- or the I^- of the solution; *e.g.*, Fe^{+++} would give a brown precipitate of $\text{Fe}(\text{OH})_3$. These interfering substances are removed by distillation.

This test is extremely sensitive; it will detect 1 part of NH_3 in 1,000,000 parts of water, or 1 mg. of NH_3 per liter. It is needless to say that such a test is "too good" to be used in a laboratory where NH_3 fumes abound.

Sodium, Na^+

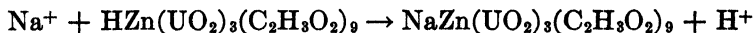
Sodium forms the univalent cation Na^+ .

The Metal.—Like potassium, sodium is too reactive to be met in the free state in analytical substances. Its compounds are widely distributed in nature and in industry.

Solubilities.—Most Na^+ salts are soluble. The nearest approach to insolubility is found in the triple acetates of uranium (see following paragraphs), the fluosilicate, the pyroantimonate, and the oxalate.

Reactions.—The following are the most important reactions used in the separation and detection of Na^+ .

Triple Uranyl Acetates.—The triple acetates of Na^+ , UO_2^{++} , and certain cations (Mg^{++} , Zn^{++} , and Co^{++}) have a surprisingly low solubility in water. They are soluble in strong acids and are decomposed by bases. Hence the precipitation is carried out in $\text{HC}_2\text{H}_3\text{O}_2$ solution. A typical equation is



The insolubility of this salt is increased by increasing the concentrations of the Zn^{++} , UO_2^{++} , and $\text{C}_2\text{H}_3\text{O}_2^-$ ions. High concentrations of H^+ increase the solubility by combining with the $\text{C}_2\text{H}_3\text{O}_2^-$ to form molecular $\text{HC}_2\text{H}_3\text{O}_2$. A high Zn^{++} concentration may be easily realized by precipitating K^+ with $\text{Zn}(\text{ClO}_4)_2$ instead of HClO_4 . Any anion precipitating UO_2^{++} would interfere—*e.g.*, OH^- , PO_4^- , C_2O_4^- , CO_3^- , etc.

Sodium Fluosilicate.— H_2SiF_6 will precipitate Na_2SiF_6 from Na^+ solutions of moderate concentration. The salt is almost insoluble in alcohol. Its solubility is only slightly increased by the presence of strong acids, for there is little tendency to remove the SiF_6^- as molecular H_2SiF_6 , which is a fairly strong acid. Na_2SiF_6 is then a good form in which to precipitate Na^+ in acid solutions from which K^+ has already been removed.

Sodium Antimonate.—A KOH solution of potassium “pyroantimonate,” $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$, precipitates Na^+ as white crystalline $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$. The formation of the precipitate may be hastened by rubbing the inside of the test tube with a stirring rod (see Supersaturated Solutions, page 10). NH_4^+ ions interfere by causing the precipitation of white antimonious acid—possibly H_3SbO_3 . Cation Groups I to IV also interfere. The reagent does not keep well, and fresh solutions should be prepared as needed.

Precipitation of NaCl by HCl.—If an Na^+ solution, not too dilute, is saturated with gaseous HCl, the Na^+ is almost completely precipitated as NaCl. This insolubility of NaCl in concentrated HCl cannot be fully accounted for in terms of the common-ion effect, even if it were assumed that the mass law could be applied to strong electrolytes. It seems likely that the HCl reacts here as a dehydrating agent, combining with the water and precipitating the NaCl. According to the solvation theory, HCl hydrate is more stable than NaCl hydrate.

Flame Reaction.—Sodium compounds color the Bunsen flame an intense yellow. This reaction is exceedingly sensitive. Many reagents dissolve enough Na^+ from the reagent bottles to cause interference, and there is enough NaCl in the insensible perspiration on the fingers to give a decided test. In other words, the test is so good that it is not worth anything at all! Many cations interfere by giving strongly colored flames (*e.g.*, Ca^{++} , Sr^{++} , and Li^+). Organic matter introduced into the solution by filter paper, etc., also interferes by burning with a yellow flame.

Detection.—The most important test in the detection of Na^+ is the precipitation of (1) a triple uranyl acetate, such as $\text{NaZn}(\text{UO}_2)_2(\text{C}_2\text{H}_3\text{O}_2)_6$. There is a minimum of interference in this test. Less important tests are the precipitation of (2) $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ and (3) Na_2SiF_6 after the removal of K^+ . (4) The flame

test may be used as confirmatory, keeping in mind the various interferences.

Potassium, K⁺

Potassium forms the univalent cation K⁺.

The Metal.—Potassium is too reactive to have any industrial uses. It is vigorously attacked by moist air and is apt to take fire when brought into contact with water. On the other hand, its compounds are frequently met with in natural and industrial materials.

Solubilities.—Most K⁺ compounds are soluble. The following salts are representative of the insoluble compounds: perchlorate, cobaltinitrite, fluosilicate, acid tartrate, etc.

Reactions.—The following are the most important reactions used in the separation and detection of K⁺.

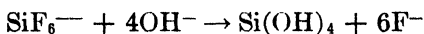
Potassium Perchlorate.—Perchloric acid, HClO₄, and its salts form with K⁺ a white precipitate of KClO₄. This precipitate is sparingly soluble in water (0.146 mole per liter at 25°) but is practically insoluble in 80 per cent alcohol. The sensitiveness of the reaction may be increased (1) by previously concentrating the solution, (2) by adding alcohol, and (3) by the common-ion effect (*i.e.*, adding an excess of the concentrated precipitant). The concentration must always be made before adding the alcohol, for heating a mixture of HClO₄ and C₂H₅OH may cause a terrific explosion.¹ This hazard is avoided by using a soluble perchlorate, as Zn(ClO₄)₂, instead of HClO₄. It is better to remove the NH₄⁺ ions, to prevent the formation of a precipitate of ammonium perchlorate, NH₄ClO₄, which is only moderately soluble (1.86 moles per liter at 25°).

Potassium Cobaltinitrite.—Sodium cobaltinitrite, Na₃Co(NO₂)₆, precipitates K⁺ as a yellow precipitate of the approximate composition K₂NaCo(NO₂)₆. This is possibly the most insoluble of the K⁺ salts. However, it cannot be formed in strongly acid solution, for free H₃Co(NO₂)₆ is unstable, or in alcoholic solutions, for the reagent is precipitated by alcohol. Another possible

¹ Probably ethyl perchlorate, C₂H₅ClO₄, is formed. This is analogous to ethyl nitrate, C₂H₅NO₃, glyceryl nitrate (nitroglycerin), C₃H₅(NO₃)₃, and cellulose nitrate (guncotton) C₁₂H₁₄O₄(NO₃)₆, all of which are high explosives. Perchloric acid also reacts explosively with many other organic materials, such as filter paper.

objection to it is that it introduces the Na^+ ion, thereby blocking the detection of this cation in the filtrate. I^- ions and other reducing agents interfere by decomposing the precipitant.

Potassium Fluosilicate.—Fluosilicic acid, H_2SiF_6 , precipitates K^+ as gelatinous K_2SiF_6 , very slightly soluble in water and insoluble in alcohol. H_2SiF_6 is a strong acid, so that the precipitate is insoluble in acids. It is decomposed in alkaline solution, forming gelatinous $\text{Si}(\text{OH})_4$.



This $\text{Si}(\text{OH})_4$ is easily mistaken for a test for K^+ .

Potassium Chloroplatinate.—Chloroplatinic acid, H_2PtCl_6 , forms with K^+ in acid solution yellow crystalline K_2PtCl_6 , slightly soluble in water, but practically insoluble in 80 per cent alcohol. NH_4^+ gives a similar reaction. The expensiveness of the reagent (about \$400 a liter) excludes this reaction from qualitative procedures.

Potassium Hydrogen Tartrate.—Tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, and sodium hydrogen tartrate, $\text{NaHC}_4\text{H}_4\text{O}_6$, precipitate K^+ as potassium hydrogen tartrate, $\text{KHC}_4\text{H}_4\text{O}_6$ (cream of tartar). $\text{KHC}_4\text{H}_4\text{O}_6$ is soluble in strong acids, owing to the formation of slightly ionized $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, and in strong bases, owing to the conversion of $\text{HC}_4\text{H}_4\text{O}_6^-$ into $\text{C}_4\text{H}_4\text{O}_6^{--}$. For these reasons, $\text{KHC}_4\text{H}_4\text{O}_6$ must be precipitated from slightly acid solution—usually $\text{HC}_2\text{H}_3\text{O}_2$ or $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$. The precipitate may form slowly, owing to supersaturation (see page 10). Vigorous agitation, or “seeding” with a minute crystal of $\text{KHC}_4\text{H}_4\text{O}_6$, will speed up the reaction.

Potassium Bismuth Thiosulfate.—Bismuth thiosulfate, $\text{Bi}_2(\text{S}_2\text{O}_3)_3$, is soluble in excess of $\text{Na}_2\text{S}_2\text{O}_3$, forming a complex ion: $\text{Bi}_2(\text{S}_2\text{O}_3)_3 + 3\text{S}_2\text{O}_3^{--} \rightarrow 2\text{Bi}(\text{S}_2\text{O}_3)_3^{--}$ (see page 371). In the presence of alcohol, this reagent forms a yellow precipitate of $\text{K}_3\text{Bi}(\text{S}_2\text{O}_3)_3$ (Carnot’s reaction). In other words, the Na^+ salt of this complex ion is soluble in alcohol, and the K^+ salt is insoluble.

Flame Reaction.—Volatile K^+ compounds give a violet color to the Bunsen flame. This reaction is masked by many other substances that give flame colors. A small amount of Na^+ will completely obscure it. However, if the flame is viewed through

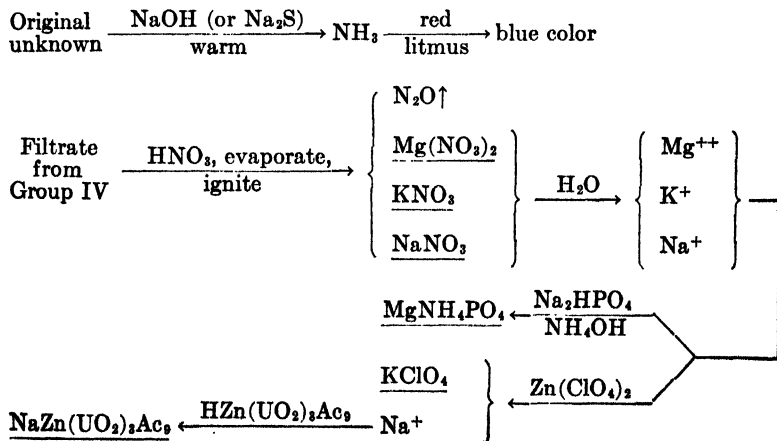
a thick cobalt glass, the yellow of the Na^+ flame will be absorbed, and the K^+ flame will appear reddish against the blue background. This is usually explained by assuming that blue glass will absorb yellow light but transmit red light. Another point of view is that any transmitted light (even blue) will appear red in contrast with the blue background.

Detection.— K^+ ions may be detected as follows: (1) By the precipitation of KClO_4 by HClO_4 or a ClO_4^- solution. The presence of alcohol makes the test more sensitive. (2) By the precipitation of $\text{K}_2\text{NaCo}(\text{NO}_2)_6$ in water solution. (3) By the violet color conferred upon the Bunsen flame. NH_4^+ salts interfere in (2) and also in (1) if the concentration of NH_4^+ is considerable. On account of the interferences of certain of the cations of previous groups, the flame test is not reliable on original samples. It is suggested that the flame test should be used only as confirmatory, preferably with KClO_4 precipitates.

ANALYSIS OF GROUP V

Separations are not necessary in many of the tests in this group, and a certain flexibility of method results. Consequently, various textbooks show many differences in procedure. The methods outlined in Tables 37 and 38 are representative.

TABLE 37.—THE PERCHLORATE-URANYL ACETATE METHOD

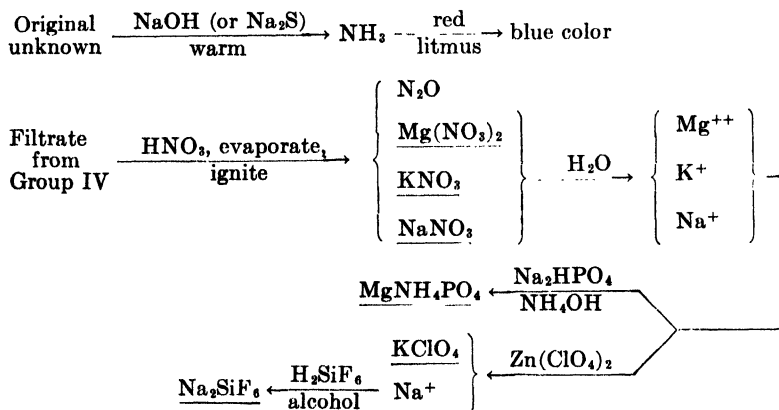


1. If Hg^{++} is present in the unknown, Na_2S , instead of NaOH , is used to evolve the NH_3 from NH_4^+ .

2. Excessive amounts of NH_4^+ are removed by evaporation with HNO_3 and ignition. Excess NH_4^+ may interfere with the tests for Mg^{++} and K^+ .

3. Flame tests may be used as confirmatory after the separation of K^+ and Na^+ as KClO_4 and $\text{NaZn}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9$.

TABLE 38.—THE PERCHLORATE-FLUOSILICATE METHOD



1. Note that the separations in the method are identical with those of the preceding method up to the separation of K^+ and Na^+ .

2. The HClO_4 solution must not be heated after adding alcohol. Dangerous explosions may occur.

3. Flame tests may be used as confirmatory after filtering out the KClO_4 and Na_2SiF_6 precipitates. Do not try flame tests on the original or upon precipitates in the presence of the HClO_4 -alcohol mother liquor.

Exercises

1. Point out some compounds of NH_4^+ that resemble K^+ more than Na^+ .
2. Explain the solubility of $\text{Mg}(\text{OH})_2$ in NH_4^+ solutions.
3. What is the purpose of the ignition-with- HNO_3 procedure in Group V?
4. What is formed when $(\text{NH}_4)_2\text{SO}_4$ is ignited?
5. Would it be possible to lose K^+ and Na^+ by igniting too strongly in the removal of NH_4^+ ?
6. With what tests for K^+ and Na^+ do NH_4^+ ions interfere?
7. How could you distinguish K_2PtCl_6 from $(\text{NH}_4)_2\text{PtCl}_6$ by means of ignition tests? $\text{KHC}_4\text{H}_4\text{O}_6$ from $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$?
8. Name three anions that form precipitates with the zinc uranyl acetate reagent for Na^+ .

9. Why is $\text{NaZn}(\text{UO}_2)_2(\text{C}_2\text{H}_3\text{O}_2)_6$ readily soluble in acids, while KClO_4 is not?

10. What anions interfere with the PtCl_6^{--} test for K^+ ?

11. Identify the following cations of Group V:

(a) A cation precipitated by Na_2CO_3 , but not by $(\text{NH}_4)_2\text{CO}_3$.

(b) A cation that gives a precipitate with $\text{Na}_2\text{Co}(\text{NO}_2)_6$ and an odor of NH_3 with NaOH .

(c) A cation that gives a precipitate with either H_2SiF_6 or HClO_4 , insoluble in 50 per cent alcohol.

(d) A cation that gives with NaOH a white precipitate, soluble in NH_4^+

12. Explain how KCl can be quantitatively converted into KNO_3 by evaporation with excess HNO_3 , and how KNO_3 can be converted into KCl by evaporation with excess HCl .

13. How many cubic centimeters of 6 M HClO_4 and 0.5 M H_2SiF_6 would be required to precipitate 78.2 mg. of K^+ and 69 mg. of Na^+ in a 50 per cent alcoholic solution.

14. Treatment of 1.49 g. of KCl in 50 per cent alcohol is made with 2 cc. of 6 M HClO_4 . How many cubic centimeters of 0.5 M H_2SiF_6 must be added to complete the precipitation of the K^+ ?

15. There is dissolved 0.12 g. of metallic magnesium in 5 cc. of 6 M HCl , and to the solution is added 25 cc. of 0.25 M Na_2HPO_4 and 5 cc. of 15 M NH_4OH . The MgNH_4PO_4 is then removed by filtration. Calculate the composition of the filtrate in moles and in grams.

16. What volume of M NaOH would be required completely to react with 0.02 mole of MgSO_4 , 0.03 mole of NH_4Cl , and 0.05 mole of KNO_3 ?

Ans.: 0.07 mole.

17. What would be the theoretical amount of 6 M HNO_3 necessary to convert 0.117 g. of NaCl into NaNO_3 ? How many moles of NO and Cl_2 would be formed?

18. There is added 10 cc. of M NaOH to 0.307 g. of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, and the mixture is evaporated to dryness. Calculate the composition of the mixture in moles of $\text{Mg}(\text{OH})_2$, Na_3PO_4 , and NaOH .

19. What weight of $\text{NaNH}_4\text{HPO}_4$ should be added to a solution containing 5 cc. of 0.5 M $\text{Mg}(\text{NO}_3)_2$ and an excess of NH_4OH and NH_4NO_3 in order completely to precipitate the Mg^{++} as MgNH_4PO_4 ? What will be the weight of the other products of the reaction?

20. What will be the composition (substances and their weights) of the precipitate obtained by mixing 0.01 mole each of MgSO_4 , BaHPO_4 , and NH_4OH , and shaking until equilibrium is reached (molar solubilities: BaSO_4 , 1.1×10^{-5} ; BaHPO_4 , 4.3×10^{-4} ; MgNH_4PO_4 , 6.3×10^{-5})?

CHAPTER XIX

GENERAL PROCEDURE IN ANION ANALYSIS

The detection of the negative groups present in an unknown mixture involves procedures quite different from those used in cation analysis. This is owing to the following reasons: (1) Many of the anion tests may be made on the original solution, without separation from other anions. (2) Separations are difficult, sometimes impracticable; for upon acidification many anions form unstable acids which are apt to be lost. (3) It is difficult to work out a procedure for the successive precipitation of the anions in groups. This has been done by certain authors, but, on the whole, the procedures are longer and require more careful technique than those in which direct tests are used.

Anion Groups and Group Reagents.—The general procedure followed in this book was proposed by Robert W. Bunsen in 1878. It consists in *classifying* (not *separating*) the anions into groups according to their reaction with certain reagents. If any group is shown to be absent, no tests are made for its constituent ions. On the other hand, when a group is indicated as present, individual tests must be made for each of its members. This method is very speedy in cases where only a few anions are present. In complex mixtures, it is not so satisfactory.

The reagents usually employed in testing for the anion groups are solutions of Ag^+ and Ba^{++} ions. In most books using this method, the reagents cited are in the form of AgNO_3 and BaCl_2 , respectively. In this book, $\text{Ba}(\text{NO}_3)_2$ is recommended instead of BaCl_2 , to obviate error due to the formation of insoluble chlorides. For example, when a solution of AgNO_3 is tested for SO_4^{--} , using BaCl_2 as the reagent, the precipitate of AgCl formed could be mistaken for BaSO_4 . When $\text{Ba}(\text{NO}_3)_2$ is used, there is no interference.

* Sometimes Ca^{++} is added to the Ba^{++} reagent. This sensitizes the precipitation of certain anions; *e.g.*, F^- , for CaF_2 is more insoluble than BaF_2 . Pb^{++} is also sometimes added for the same purpose.

In addition to the preceding, two other groups are recognized, *viz.*: Group VI (silicates) and Group VII (organic anions). These two groups do not give distinctive reactions with Ag^+ and Ba^{++} ions and are not amenable to classification by these reagents.

Organic anions (Group VII), as a rule, are not included in courses in inorganic analysis, for the methods involved in their detection are basically different from those used for inorganic anions.

There are several other systems of reactions that may be used to indicate the presence or absence of certain groups of anions.

Silver Salts and Their Colors.—The colors of the Ag^+ salts of the anions are frequently distinctive, and valuable information

TABLE 39.—SOLUBILITIES AND COLORS OF SILVER SALTS

Soluble in H_2O	Insoluble in H_2O , soluble in dil. HNO_3	Insoluble in HNO_3
AgNO_3 } very soluble AgClO_4 } Ag_2SO_4 } sparingly AgNO_2 } soluble $\text{AgC}_2\text{H}_3\text{O}_2$ }	Ag_2CO_3 (white) $\text{Ag}_2\text{C}_2\text{O}_4$ (white) Ag_2SO_3 (white) $\text{Ag}_2\text{S}_2\text{O}_3$ (white) AgBO_2 (white) Ag_3PO_4 (yellow) Ag_3AsO_4 (brown) Ag_3AsO_3 (yellow) Ag_2CrO_4 (maroon) Ag_2O (brown)	AgCl (white) AgBr (cream) AgI (yellow) AgSCN (white) $\text{Ag}_4\text{Fe}(\text{CN})_6$ (white) $\text{Ag}_3\text{Fe}(\text{CN})_6$ (orange) Ag_2S (black)

may be had from the reaction given when AgNO_3 is added to the solution of the unknown. For this reason, the most important of the Ag^+ salts are listed in Table 39, along with their solubilities and colors. The student should refer to this table frequently, until he is perfectly familiar with the facts.

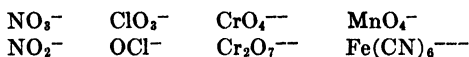
Significance of Acidity.—As already stated, the acids corresponding to certain anions are unstable, so that these anions can hardly be expected to be present in a solution acidic to indicators, particularly when it is open to the air for some time. These acids may be grouped as shown in the table on page 316.

Significance of Oxidizing and Reducing Agents.—The presence of an active oxidizing agent in a mixture excludes the presence of most reducing agents; and, vice versa, the presence of an

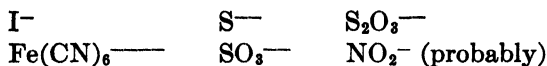
active reducing agent excludes the presence of most oxidizing agents. To illustrate: SO_3^{--} ions could not be present in a solution containing HMnO_4 ; nor could MnO_4^- ions be present in a solution containing SO_3^{--} .

Volatile acids	Unstable acids	Acids oxidized by air	Acid attacking glass
H_2S HCN	HNO_2 H_2CO_3 H_2SO_3 $\text{H}_2\text{S}_2\text{O}_3$ HClO_3 H_2SiO_3	HI H_2S HBr $\text{H}_4\text{Fe}(\text{CN})_6$ HNO_2 H_2SO_3	HF

The presence of strong oxidizing agents in an unknown may be detected by adding a solution of MnCl_2 in concentrated HCl and warming gently. The oxidation of the Mn^{++} with the formation of a brown color¹ indicates the presence of one or more of the following anions:



The presence of strong reducing agents is indicated by the formation of a dark blue color when a mixture of FeCl_3 and $\text{K}_3\text{Fe}(\text{CN})_6$ * is added to the acidified solution of the unknown. An immediate blue color² indicates one or more of the following anions:



¹ The composition of the compound giving the brown color is in doubt. Some authorities consider it manganic chloride, MnCl_3 ; but others consider it manganese tetrachloride, MnCl_4 , or its hydrolytic product $\text{MnO}_2 \cdot x\text{H}_2\text{O}$.

* If the $\text{K}_3\text{Fe}(\text{CN})_6$ solution is not freshly prepared, it will contain some $\text{Fe}(\text{CN})_6^{--}$ anions, and a slight blue color will appear in the absence of reducing agents.

² The blue color may be explained as due to: (1) the reduction of Fe^{+++} to Fe^{++} with the subsequent formation of Turnbull's blue, $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$; or (2) the reduction of $\text{Fe}(\text{CN})_6^{--}$ to $\text{Fe}(\text{CN})_6^{--}$, with the subsequent formation of Prussian blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. The latter seems to be the better explanation, for $\text{Fe}(\text{CN})_6^{--}$ is more readily reduced than Fe^{+++} . That is, $\text{Fe}(\text{CN})_6^{--}$ is the better oxidizing agent.

The application of the principle that oxidizing and reducing agents cannot coexist in the same material is subject to the following limitations. (1) The anions of oxidizing and reducing acids may coexist in neutral or alkaline materials; *e.g.*, a mixture of KNO_3 and KBr is quite stable until an acid is added. As mentioned before, it seems that in many cases oxidizing and reducing action is inherent in the un-ionized acids and not in the anions themselves. (2) Weak oxidizing agents and weak reducing agents can exist side by side without appreciable change; *e.g.*, oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, and dilute HNO_3 ; HBr and HNO_2 ; MnO_2 and Na_2O_2 in alkaline medium. It follows that judgment must be used in applying this principle in anion analysis.

Information from Solubility Considerations.—In the case of solids, the solubility of the material in water, acids, etc., combined with a knowledge of the cations present, gives valuable information about the anions that may be present. For example, a water-soluble unknown containing Ba^{++} cannot contain AsO_3^- , AsO_4^- , PO_4^- , BO_3^- , C_2O_4^- , F^- , CO_3^- , SiO_3^- , SO_4^- , or $\text{C}_4\text{H}_4\text{O}_6^-$, for the Ba^{++} salts of all these anions are insoluble in water (see Solubility Table). If the unknown is also insoluble in dilute HNO_3 or HCl , it can contain only SO_4^- , F^- , or SiF_6^- .

This approach is of no value in case the only cations present are Na^+ , K^+ , and NH_4^+ . These cations form soluble salts with practically all anions, so that no possibilities are eliminated.

The use of this principle may be misleading in certain cases where compounds of low ionization (including complex ions) are formed. For example, SO_4^- may be present in a water-soluble material containing Pb^{++} , if a soluble acetate is present; as $\text{PbSO}_4 + \text{excess NaC}_2\text{H}_3\text{O}_2$. Another case— $\text{MgCO}_3\text{-NH}_4\text{Cl}$ mixture is soluble in water, although MgCO_3 alone is insoluble.

Another limitation to this principle is that many substances tend to decrease in solubility upon ignition. For examples, precipitated PbCrO_4 is soluble in dilute HNO_3 , but ignited PbCrO_4 is insoluble; precipitated MgCO_3 dissolves easily in $\text{HC}_2\text{H}_3\text{O}_2$, but the mineral MgCO_3 dissolves slowly even in dilute HCl .

Interference by Cations.—The cations of Groups I to IV (sometimes called the *heavy metals*) interfere in anion analysis in several ways: (1) They form insoluble precipitates with many of the

anions, masking the effects of certain test reagents. (2) Some of them are colored and reduce the visibility of the test reactions. (3) Sometimes they react with the "wrong end" (*i.e.*, the anion) of the reagent, giving reactions that might be taken to be positive tests. For example, when a solution containing Ag^+ ions is tested for SO_4^{--} by means of BaCl_2 solution, the precipitate of AgCl

TABLE 40.—REACTIONS OF ANIONS WITH CONCENTRATED SULFURIC ACID

A gas is liberated			No effect
Color	Reactions of the gas	Anion indicated	
Colorless	White precipitate with AgNO_3	Cl^-	Anions that may be present: PO_4^{--} , AsO_3^{--} , AsO_4^{--} , CrO_4^{--} , BO_3^{--} , MnO_4^- , SO_4^{--} , SiO_3^{--}
	Brown stain on $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ paper	S^{--}	
	Odor of $\text{HC}_2\text{H}_3\text{O}_2$; characteristic odor in presence of alcohol	$\text{C}_2\text{H}_3\text{O}_2^-$	
	SO_2 odor { No S is precipitated	SO_3^{--}	
	{ S is precipitated	$\text{S}_2\text{O}_3^{--}$ or S^{--}	
	White precipitate with $\text{Ca}(\text{OH})_2$	CO_3^{--} or $\text{C}_2\text{O}_4^{--}$	
	Tube is etched; turbidity on drop of water	F^-	
	Gas burns with a blue flame	$\text{C}_2\text{O}_4^{--}$, $\text{Fe}(\text{CN})_6^{--}$, $\text{Fe}(\text{CN})_6^{--}$	
	Disagreeable odor and separation of S	SCN^-	
	Yellow color in H_2SO_4 ; explosion upon warming	ClO_3^-	
Greenish-yellow	Creamy precipitate with AgNO_3 ; red litmus paper bleached	Br^-	—
Brown	Brown color in drop of FeSO_4	NO_2^- , NO_3^-	
Purple	Blue color with starch paper	I^-	

may be mistaken for BaSO_4 . Again, Ba^{++} , Pb^{++} , etc., interfere with the brown ring test for NO_3^- by forming precipitates of insoluble sulfates with the FeSO_4 and H_2SO_4 solution.

These interfering cations are usually removed by adding an excess of Na_2CO_3 , leaving all the anions in the practically neutral filtrate. The excess CO_3^{--} may interfere to some extent by effervescence upon acidification. The aqueous solution obtained by

fusing a solid with Na_2CO_3 and extracting the melt with water is analogous. This "prepared solution" may be used for the tests for all anions except CO_3^{--} , OH^- , etc.

Warning is given that even high-grade Na_2CO_3 frequently contains Cl^- , and the reagent should always be tested for this impurity.

Heating with Concentrated Sulfuric Acid.—Certain anions show fairly distinctive reactions when their solid salts are heated with 90 per cent H_2SO_4 (see Table 40).

Anions Detected during Cation Analysis.—Certain anions may be detected by their behavior during cation analysis, *viz.*, AsO_3^{--} , AsO_4^{--} , CrO_4^{--} , $\text{Cr}_2\text{O}_7^{--}$, and MnO_4^- . See the individual anions for further details.

Exercises

1. Contrast the detection of anions with the detection of cations in three respects.

2. How would you separate the following anion groups:

- (a) Group I and Group V.
- (b) Group I and Group III.
- (c) Group III and Group IV.
- (d) Group II and Group I.
- (e) Group V and Group III.

3. Are any cations strong enough oxidizing agents to interfere with the $\text{MnCl}_2\text{-HCl}$ test for oxidizing anions?

4. Name the cations that give blue colors with the $\text{FeCl}_3\text{-K}_3\text{Fe}(\text{CN})_6$ mixture.

5. Name sets of oxidizing and reducing anions that may coexist in the same solution.

6. What is the general procedure for removing the heavy metals preparatory for the anion tests?

7. A white solid, insoluble in water, is soluble in dilute HNO_3 . Pb^{++} and As^{+5} are detected in Cation Group II—all other tests being negative. A sample of the solid dissolved in dilute HCl liberates I_2 from KI solution. Interpret the analysis.

8. A yellow powder is insoluble in water but dissolves in dilute HNO_3 , giving an orange solution. Cr^{+++} and Ba^{++} are detected in cation analysis. Identify the material.

9. A white K^+ salt is soluble in water, forming a colorless solution. This solution gives a yellow precipitate with AgNO_3 solution, which turns brown upon the addition of H_2O_2 . Identify the salt.

10. Name four anions that could be present in a solution containing SnCl_2 .

11. A colorless solution gives a brown color when warmed with a saturated MnCl_2 solution in concentrated HCl . Which of the following anions can be present: I^- , NO_3^- , $\text{C}_2\text{H}_3\text{O}_2^-$, $\text{C}_2\text{O}_4^{--}$, AsO_4^{--} ?

12. A colorless solution gives a brown color with the $\text{MnCl}_2\text{-HCl}$ reagent and a blue color with the $\text{FeCl}_3\text{-K}_3\text{Fe}(\text{CN})_6$ reagent. Suggest an anion that might be responsible for both reactions.

13. A neutral solution gives with AgNO_3 a yellow precipitate, insoluble in HNO_3 , soluble in NH_4OH . What anion is suggested?

14. A neutral solution gives with AgNO_3 a brown precipitate, partially soluble in dilute HNO_3 , leaving a black residue. Upon careful neutralization of the filtrate, a deep-red precipitate appears. What two anions are suggested?

15. A colorless acid solution gives no reaction with concentrated H_2SO_4 . What anions are possible?

16. An acidic unknown gives no darkening with the $\text{MnCl}_2\text{-HCl}$ reagent. What anions can be present?

17. A concentrated solution, upon warming with 90 per cent H_2SO_4 , gives off a colorless, odorless, noninflammable gas. What anion is indicated?

18. A white powder is warmed with 90 per cent H_2SO_4 , and a gas with an acid odor is evolved. This gas gives no reaction with AgNO_3 solution. What anion is suggested?

CHAPTER XX

ANION GROUP I

This group contains the anions whose Ag^+ salts are insoluble in water and cold dilute HNO_3 , and whose Ba^{++} salts are soluble in water. The membership is as follows:

Chloride, Cl^-	Ferrocyanide, $\text{Fe}(\text{CN})_6^{4-}$
Bromide, Br^-	Ferricyanide, $\text{Fe}(\text{CN})_6^{3-}$
Iodide, I^-	Sulfide, S^{2-}
Cyanide, CN^-	[Hypochlorite, OCl^-]
Thiocyanate, SCN^-	

The brackets used in the case of the hypochlorite ion indicate that it is usually not considered in analyses.

The properties of the CN^- and SCN^- ions parallel those of the halide ions very closely. For this reason, they are sometimes called *halogenoids*. The reactions of the ions of the halogen-halogenoid group are so similar that separations are difficult. In some cases, they are not attempted at all.

CHLORIDE

The Acid.—Pure hydrogen chloride is a colorless gas, boiling at -8.5° . It is prepared by (1) the action of a high-boiling acid on chlorides, and (2) the direct combination of hydrogen and chlorine. Gaseous HCl is very soluble in water, 1 l. of water dissolving about 450 l. of the gas. The concentrated HCl of the laboratory is about 12 molar, and the dilute acid is about 6 molar. HCl cannot be separated from water by distillation. The component— HCl or water—present in excess distills out faster than the minor component, until the residue in the container is about 20 per cent HCl , which then distills at 110° without change in composition.

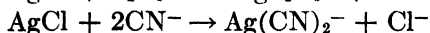
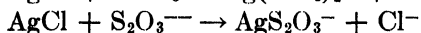
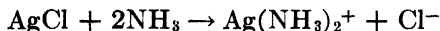
Volatilization with High-boiling Acids.—Concentrated H_2SO_4 (boiling point, 330°) and concentrated H_3PO_4 (boiling point, 230°) react with most chlorides,¹ forming gaseous HCl ; *e.g.*, $\text{Cl}^- +$

¹ AgCl and Hg_2Cl_2 are scarcely affected by these reagents.

$\text{H}_2\text{SO}_4 \rightleftharpoons \text{HCl} + \text{HSO}_4^-$. The relative lengths of the arrows indicate that the effect is due, not to the strength (*i.e.*, the ionization) of the added acid, but to the greater volatility of the HCl.

Solubilities.—All chlorides are soluble in water except AgCl, Hg_2Cl_2 , Cu_2Cl_2 , SbOCl, BiOCl, and a few chlorides of the gold-platinum group. SbOCl and BiOCl are soluble in dilute HCl. Lead chloride, PbCl_2 , is only slightly soluble in cold water, but fairly soluble in hot water.

Silver Chloride.—One of the most insoluble chlorides is AgCl (*cf.* page 178). It is a curdy, white precipitate, turning a slate-blue color under the influence of white light. It is insoluble in dilute HNO_3 , but soluble in NH_3 and alkaline thiosulfate and cyanide solutions.



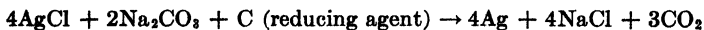
Silver chloride is partially transposed by NaOH solution, the amount increasing with the concentration of the OH^- ions.



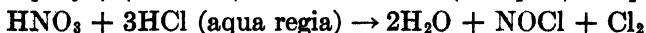
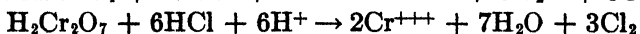
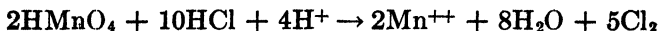
Silver chloride may be brought into solution for analytical purposes by treating it with metallic zinc in the presence of dilute H_2SO_4 .



The metallic silver is separated by filtration, and Cl^- ions are detected in the solution in the regular way. Silver chloride is also decomposed by fusion with Na_2CO_3 in the presence of a reducing agent, such as flour.



Oxidation.—Concentrated HCl reacts as a reducing agent toward strong oxidizing agents, such as HMnO_4 and $\text{H}_2\text{Cr}_2\text{O}_7$, with the liberation of Cl_2 ; *e.g.*,



Since chlorides are not oxidized by the most powerful alkaline

oxidizing agents (*e.g.*, Na_2O_2), it appears that the reducing action is due to the HCl molecule and not to the Cl^- ion.

With concentrated H_2SO_4 , no Cl_2 is evolved, for HCl is not a strong enough reducing agent to reduce H_2SO_4 .

Free Chlorine.—Free chlorine is a greenish-yellow gas, boiling at -33.6° . It is slightly soluble in water, but readily soluble in certain organic solvents, such as carbon tetrachloride, CCl_4 , with which it forms a colorless solution. Chlorine is soluble in alkaline solutions, such as NaOH and Na_2CO_3 , forming as initial products a mixture of chloride and hypochlorite, thus: $\text{Cl}_2 + 2\text{OH}^- \rightleftharpoons \text{Cl}^- + \text{OCl}^- + \text{H}_2\text{O}$. If this mixture is heated and allowed to become acid, the hypochlorite changes into chlorate and chloride: $3\text{OCl}^- \rightarrow \text{ClO}_3^- + 2\text{Cl}^-$.

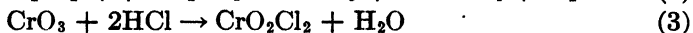
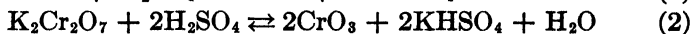
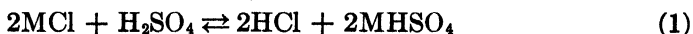
Chromyl Chloride.—When a dry chloride (excepting AgCl and Hg_2Cl_2) is heated with $\text{K}_2\text{Cr}_2\text{O}_7$ in the presence of concentrated H_2SO_4 , chromyl chloride, CrO_2Cl_2 , is formed. This is a dark red liquid, boiling at 116° , and may be distilled out of the reaction mixture. Bromides, iodides, etc., do not form analogous compounds but are completely oxidized to Br_2 , I_2 , etc., and therefore carry no chromium into the distillate.

When CrO_2Cl_2 comes into contact with the water, it is hydrolyzed, forming Cl^- , CrO_4^{--} , etc.



The presence of CrO_4^{--} ions in the diluted distillate may be shown by the formation of yellow BaCrO_4 upon the addition of Ba^{++} ions and an excess of $\text{C}_2\text{H}_3\text{O}_2^-$ to repress the H^+ ions.

The formation of CrO_2Cl_2 is a stepwise reaction. Representing the chloride by MCl , the equations may be written:



Neither reaction (1) nor (2) proceeds to completion of itself; but reaction (3) goes to practical completion upon boiling and, by using up the products of reactions (1) and (2), carries them also to completion.

Detection.—The following procedures are used for the detection of the Cl^- ion.

1. *Precipitation of Silver Chloride.*—The most sensitive test for Cl^- ions is the formation of white, curdy AgCl , insoluble in

dilute HNO_3 , but soluble in NH_3 , $\text{S}_2\text{O}_3^{--}$, and CN^- solutions. CN^- , SCN^- , and $\text{Fe}(\text{CN})_6^{--}$ ions also form white precipitates with Ag^+ , with about the same solubilities. Other members of Anion Group I interfere by forming colored precipitates that mask any AgCl . In other words, the white, curdy Ag^+ precipitate is a test for Cl^- ions only when *interfering ions are known to be absent*.

2. Chromyl Chloride Method.—The formation of a precipitate of yellow BaCrO_4 in the distillate obtained when the *solid* unknown is heated with $\text{K}_2\text{Cr}_2\text{O}_7$ and concentrated H_2SO_4 is a sensitive test for “straight” chlorides, but it cannot be recommended in the case of mixtures, particularly when a reducing agent is present. Nitrate interferes by forming volatile $\text{CrO}_2(\text{NO}_3)_2$.

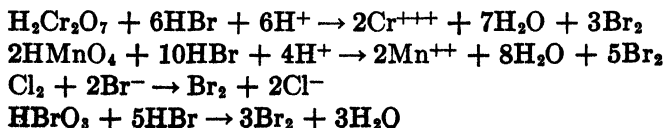
BROMIDE

The Acid.—Hydrogen bromide, HBr , is a colorless gas, very soluble in water, forming a solution generally known as *hydrobromic acid*. Pure HBr is usually prepared by adding SO_2 to Br_2 solution, thus: $\text{Br}_2 + 2\text{H}_2\text{O} + \text{SO}_2 \rightarrow 2\text{HBr} + \text{H}_2\text{SO}_4$. The HBr is separated by distillation. It is a very strong acid—one of the “completely ionized” group.

Volatility.—Like HCl , HBr is volatile and may be separated from high-boiling acids by distillation. H_2SO_4 cannot be used; for, as will be seen below, it oxidizes HBr .

Solubilities.—All bromides are soluble in water except AgBr , Hg_2Br_2 , Cu_2Br_2 , BiOBr , and SbOBr . BiOBr and SbOBr are readily soluble in dilute acids. PbBr_2 is slightly soluble in cold water, but fairly soluble in hot water.

Oxidation of Hydrobromic Acid.— HBr is a more active reducing agent than HCl and therefore is oxidized, not only by the oxidizing agents that oxidize HCl , but also by certain others. HBr is active enough to reduce concentrated H_2SO_4 to H_2SO_3 , H_3AsO_4 to H_3AsO_3 , and $\text{Fe}(\text{CN})_6^{--}$ to $\text{Fe}(\text{CN})_6^{--}$. The oxidation products of HBr are H_2O and Br_2 . For example,



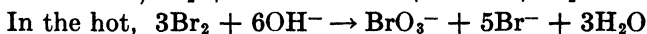
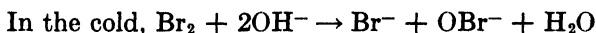
Nitrous acid is not strong enough as an oxidizing agent to oxidize HBr (*cf.* HI , page 327).

Silver Bromide.— Br^- ions are thrown down by Ag^+ ions as AgBr , a curdy, yellow precipitate, insoluble in dilute HNO_3 . It is slightly soluble in NH_3 solution—much less than is AgCl . It dissolves readily in NaCN and $\text{Na}_2\text{S}_2\text{O}_3$, forming the complex ions $\text{Ag}(\text{CN})_2^-$ and AgS_2O_3^- . Like AgCl , AgBr is darkened by light.

Silver bromide is only slightly transposed by NaOH —much less than is AgCl . With dilute NaOH , the effect is negligible. This difference is due to the fact that AgBr is much less soluble in water than is AgCl , giving too small a concentration of Ag^+ ions to react appreciably with OH^- ions.

Free Bromine.—Free bromine is a red-brown liquid, boiling at 58.8° . It is only slightly soluble in water but is readily soluble in organic solvents, such as alcohol, ether, carbon disulfide, carbon tetrachloride, and chloroform. The color of the solution ranges from yellow to brown, depending on the concentration of the bromine.

Bromine is soluble in solutions of the alkaline hydroxides and carbonates. The product formed depends upon the temperature to a large extent.



The reaction with NH_3 solution is unique.



Bromine displaces I_2 from I^- solutions: $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$.

Detection.—The following reactions are used for the detection of Br^- ions.

1. *Formation of AgBr .*—The Br^- ion reacts with Ag^+ to form curdy, cream-colored AgBr , insoluble in dilute HNO_3 , slightly soluble in NH_3 solution, and readily soluble in $\text{S}_2\text{O}_3^{2-}$ and CN^- solutions. It is not so soluble in these last solvents as is AgCl . I^- and other ions of Anion Group I interfere.

2. *Displacement of Br^- Ions by Cl_2 .*—Free chlorine oxidizes Br^- to Br_2 : $2\text{Br}^- + \text{Cl}_2 \rightarrow \text{Br}_2 + 2\text{Cl}^-$. The liberated bromine may be extracted by organic solvents (ether, carbon tetrachloride,

etc.), giving a yellow-to-red color, depending upon the amount of bromine. It should be noted that Cl_2 does not oxidize Br_2 to BrO_3^- .

3. Color Formation with Organic Substances.—When HBr is oxidized to Br_2 in the presence of fluorescein (yellow), the latter is oxidized to eosin (red). Certain other organic materials show analogous color changes.

IODIDE

The Acid.—Hydrogen iodide, HI , is a colorless gas, boiling at -35.5° . It is very soluble in water, forming a solution of hydriodic acid.

A solution of HI may be conveniently prepared by the following methods: (1) A suspension of I_2 in water is saturated with H_2S : $\text{I}_2 + \text{H}_2\text{S} \rightarrow 2\text{HI} + \text{S}$. The sulfur is removed by filtration, and the solution is concentrated by distillation. (2) An iodide is mixed with a nonoxidizing acid, such as H_3PO_4 , and HI is distilled from the mixture: $2\text{NaI} + \text{H}_3\text{PO}_4 \rightarrow 2\text{HI} + \text{Na}_2\text{HPO}_4$. (3) Phosphorus tri-iodide is hydrolyzed by water: $2\text{P} + 3\text{I}_2 \rightarrow 2\text{PI}_3$; and $\text{PI}_3 + 3\text{HOH} \rightarrow 3\text{HI} + \text{H}_3\text{PO}_3$. Again the HI is separated by distillation.

Solubilities.—The solubilities of the iodides closely parallel those of the chlorides and bromides: AgI , Hg_2I_2 , and Cu_2I_2 are insoluble in water and in dilute, nonoxidizing acids; BiOI and SbOI are insoluble in water but soluble in acids; and PbI_2 is slightly soluble in cold water but fairly soluble in hot water (*cf.* pages 322, 324). In addition to these, HgI_2 is insoluble in water but soluble in hot dilute acids.

Silver Iodide.—This is a yellow, curdy solid. It is so insoluble in water that the concentration of Ag^+ ions in its saturated solution is too small to react appreciably with NH_3 . It will dissolve, however, in $\text{S}_2\text{O}_3^{2-}$ and CN^- solutions.

Cupric and Cuprous Iodides.—Solutions of I^- ions react with Cu^{++} ions, forming a white precipitate of Cu_2I_2 in a brownish solution containing I_2 . Possibly, cupric iodide is formed as an unstable intermediate product.

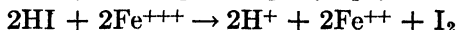
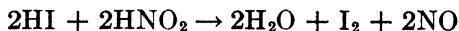


In the presence of reducing agents, no free I_2 is formed; *e.g.*,

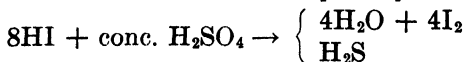
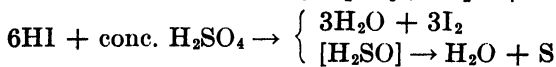
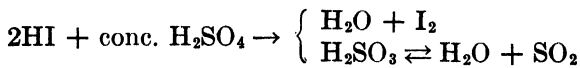


Mercuric Iodide.—Solutions of HgCl_2 form with I^- ions a scarlet-red precipitate of HgI_2 , soluble in excess of I^- ions: $\text{HgI}_2 + 2\text{I}^- \rightarrow \text{HgI}_4^{2-}$ (*cf.* page 190).

Oxidation.—Hydriodic acid is a vigorous reducing agent, taking up oxygen and forming H_2O and I_2 . It reacts with all the agents that oxidize HCl and HBr and also with certain agents that do not; *e.g.*,

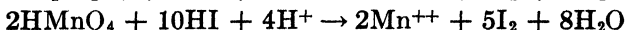
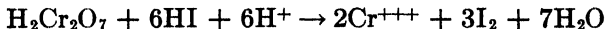


The high activity of HI as a reducing agent appears in its reactions with concentrated H_2SO_4 , which it reduces successively through the following stages: $\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{SO}_3$ (or SO_2) $\rightarrow \text{S} \rightarrow \text{H}_2\text{S}$. Equations are:



Both Cl_2 and Br_2 displace I_2 from iodide solutions, thus: $2\text{I}^- + \text{Cl}_2 \rightarrow \text{I}_2 + 2\text{Cl}^-$. Displacements, it should be remembered, are really oxidation-reduction reactions.

The $\text{Cr}_2\text{O}_7^{2-}$ ion is reduced by HI in the presence of dilute H_2SO_4 , and the MnO_4^- ion is reduced by HI even in dilute $\text{HC}_2\text{H}_3\text{O}_2$ buffered by excess $\text{C}_2\text{H}_3\text{O}_2^-$ ions.



These reactions are striking in view of the fact that the oxidizing action of $\text{H}_2\text{Cr}_2\text{O}_7$ and HMnO_4 and the reducing action of HI are reduced so much by lowering the acidity of the solution. HCl and HBr are hardly affected at all by these oxidants.

Free Iodine.—Iodine is a steel-gray solid, giving off purple fumes upon warming. It is slightly soluble in water but much more soluble in iodide solutions, owing to the formation of the tri-iodide complex ion: $\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$. Iodine is soluble in alcohol and ether, forming brown solutions, and in carbon disulfide,

carbon tetrachloride, and chloroform, giving violet solutions. It is soluble in basic solutions, similar to Cl_2 and Br_2 :

In the cold, $\text{I}_2 + 2\text{OH}^- \rightleftharpoons \text{OI}^-$ (hypoiodite) $+ \text{I}^- + \text{H}_2\text{O}$

In the hot, $3\text{I}_2 + 6\text{OH}^- \rightarrow \text{IO}_3^-$ (iodate) $+ 5\text{I}^- + 3\text{H}_2\text{O}$

The blue color formed with starch is due to the I_3^- ion and not to free I_2 .

Detection.—The formation with AgNO_3 of a yellow precipitate, insoluble in HNO_3 and in NH_4OH , is not sufficiently distinctive to be a conclusive test for the I^- ion. The most reliable reactions are color reactions with free iodine. The I^- ion is therefore converted into I_2 by an oxidizing agent (Cl_2 or HNO_3 , usually). (1) With CS_2 , CHCl_3 , and CCl_4 , I_2 forms violet solutions. (2) With starch paste in the presence of an iodide, it forms a blue color, disappearing upon heating, but returning upon cooling.

CYANIDE

The cyanide group, CN^- , was formerly called the *prusside group*, corresponding to "prussic acid," HCN .

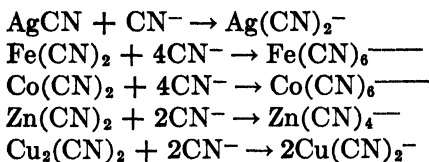
Cyanides have been highly publicized by writers of detective fiction as potent and mystic instruments of death. Without doubt, cyanides should be handled with care. But the student is reminded that many other of the reagents of the analytical laboratory are poisonous— Hg^{++} solutions, for example. Statistics show that the gas H_2S has the highest mortality record.

The Acid.—Hydrocyanic acid, HCN , is a colorless liquid, boiling at 26.5° , with an odor suggesting bitter almonds. It is soluble in water, forming a solution that slowly changes to ammonium formate: $\text{HCN} + 2\text{H}_2\text{O} \rightarrow \text{NH}_4\text{CHO}_2$.

Hydrocyanic acid is a very weak acid. The ionization constant is 7×10^{-10} . That is, a 0.1 molar solution is only 0.006 per cent ionized. As a result, HCN is displaced from CN^- solutions upon acidification.

Solubilities.—The cyanides of K^+ , Na^+ , Ca^{++} , Sr^{++} , and Hg^{++} are soluble. $\text{Ba}(\text{CN})_2$ is slightly soluble. Other cyanides are insoluble. On account of the weakness of HCN as an acid, cyanides are largely hydrolyzed: $\text{CN}^- + \text{HOH} \rightleftharpoons \text{HCN} + \text{OH}^-$. Cyanide solutions slowly change to formates: $\text{CN}^- + 2\text{HOH} \rightarrow \text{HCO}_2^- + \text{NH}_3$.

A number of cyanides insoluble in water are soluble in excess CN^- ions, forming complex anions, some of which are very stable.



Alkaline Cyanides.—Sodium and calcium cyanides are extensively used in the extraction of gold and silver from their ores.

Sodium cyanide is manufactured by the following methods. (1) In the Castner process, metallic sodium, charcoal, and ammonia are reacted in steel pots at a high temperature: $2\text{Na} + 2\text{C} + 2\text{NH}_3 \rightarrow 2\text{NaCN} + 3\text{H}_2$. (2) In the Schlempe process, HCN formed by the destructive distillation of beet sugar residues is combined with NaOH: $\text{HCN} + \text{NaOH} \rightarrow \text{NaCN} + \text{H}_2\text{O}$.

The use of NaCN in metallurgical operations has been largely superseded by calcium cyanide, formed from calcium cyanamide: $\text{CaC}_2 + \text{N}_2$ (in electric oven) $\rightarrow \text{CaCN}_2 + \text{C}$; and $\text{CaCN}_2 + \text{C} \rightarrow \text{Ca}(\text{CN})_2$.

In the laboratory, NaCN remains the important source material for the CN^- ion.

Silver Cyanide.—Silver cyanide, AgCN, is formed as a white precipitate when an excess of Ag^+ ions is added to a CN^- solution. No precipitate appears so long as CN^- ions are in excess, for AgCN is soluble in CN^- , forming the complex ion $\text{Ag}(\text{CN})_2^-$. AgCN is insoluble in dilute HNO_3 but perceptibly soluble in concentrated HNO_3 .

Separation from Other Anions.—Advantage is taken of the low ionization and volatility of HCN to separate CN^- from other anions. If a stream of gaseous CO_2 is passed through a solution, the CN^- will be swept out as HCN. H_2CO_3 solution gives a sufficient concentration of H^+ ions to convert CN^- largely into HCN, which is swept out by the excess CO_2 , as follows: $\text{CN}^- + \text{H}^+ \rightleftharpoons \text{HCN}$ (dissolved) $\rightleftharpoons \text{HCN}$ (gas). The HCN thus evolved may be caught in a solution of NaOH, and the test for CN^- made by one of the following methods.

Detection.—The CN^- ion is detected by transforming it into an anion which has a more distinctive action.

Prussian Blue Test.—When a CN^- solution is treated with a little Fe^{++} and an excess of OH^- ions (*e.g.*, NaOH) and boiled, $\text{Fe}(\text{CN})_6^{4-}$ is formed. This complex cyanide may be tested for by acidifying with HCl and adding a little FeCl_3 , forming a precipitate of Prussian blue (see page 257).

Ferric Thiocyanate Test.—When a solution containing CN^- ions is evaporated with a polysulfide, such as $(\text{NH}_4)_2\text{S}_x$ or K_2S_x , the SCN^- ion is formed (see page 258). This ion may be detected by its formation of a deep red color with FeCl_3 .

In addition to the preceding tests, there are several reactions with organic reagents that are used for the detection of CN^- ions. For further details, see more advanced textbooks.

THIOCYANATE

The name *thiocyanate* denotes a cyanate group in which the oxygen has been replaced by sulfur, *e.g.*, as in KOCN and KSCN . The ionic formula is sometimes written " SCN^- ," sometimes " CNS^- ." The " SCN^- " seems preferable, for it appears that in most cases the sulfur atom is situated in the molecule between the cationic group and the carbon, *e.g.*, as in HSCN , $\text{C}_2\text{H}_5\text{SCN}$, etc.

The Acid.—Thiocyanic acid, HSCN , is a colorless liquid, boiling at 85° . In the free state, it tends to decompose, and its dilute solutions are only moderately stable. In point of ionization, dilute HSCN is about as strong as HCl .

Preparation.—Thiocyanates are formed as follows: (1) By the addition of sulfur to the CN^- ion: $\text{CN}^- + \text{S} \rightarrow \text{SCN}^-$. (2) By the sulfonation of CN^- ions by thiosulfates: $\text{S}_2\text{O}_3^{2-} + \text{CN}^- \rightarrow \text{SO}_3^{2-} + \text{SCN}^-$. Ammonium thiocyanate, the most important of the thiocyanates, is formed when (3) a mixture of carbon disulfide and NH_4OH react in alcoholic solution: $\text{CS}_2 + 2\text{NH}_3 \rightarrow \text{NH}_4\text{SCN} + \text{H}_2\text{S}$.

Solubilities.—All the thiocyanates are soluble in water except AgSCN , $\text{Hg}(\text{SCN})_2$, and $\text{Cu}_2(\text{SCN})_2$. $\text{Pb}(\text{SCN})_2$ resembles PbCl_2 in being sparingly soluble in cold water but fairly soluble in hot water.

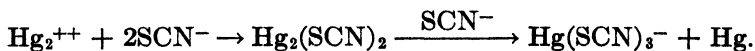
Reactions.—In most of its reactions, the SCN^- ion resembles the Cl^- ion. It is, therefore, another halogenoid.

Silver Thiocyanate.— AgSCN is a white, curdy solid, insoluble in dilute HNO_3 , but soluble in NH_3 solution.

Mercuric Thiocyanate.— $\text{Hg}(\text{SCN})_2$ is a white salt, best formed from $\text{Hg}(\text{NO}_3)_2$ solution. HgCl_2 gives too low a concentration

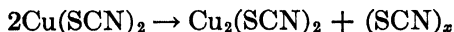
of Hg^{++} ions for the reaction with SCN^- ions to proceed completely. $\text{Hg}(\text{SCN})_2$ is easily soluble in excess of SCN^- ions, forming a complex anion, possibly $\text{Hg}(\text{SCN})_3^-$.

Mercurous Thiocyanate.—When dilute KSCN is added to dilute $\text{Hg}_2(\text{NO}_3)_2$, white $\text{Hg}_2(\text{SCN})_2$ is formed. When the order of mixing is reversed—*i.e.*, when SCN^- ions are in excess—a precipitate of black mercury is obtained.

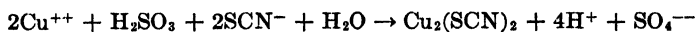


The compound is evidently not very stable.

Cuprous Thiocyanate.—When Cu^{++} and SCN^- ions are mixed, a green solution is obtained which seems to contain black cupric thiocyanate. The salt is unstable, and decomposes gradually into white, insoluble cuprous salt and thiocyanogen.

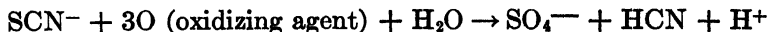


The thiocyanogen separates as a gummy mass. In the presence of a reducing agent, such as H_2SO_3 , cuprous thiocyanate is directly precipitated.

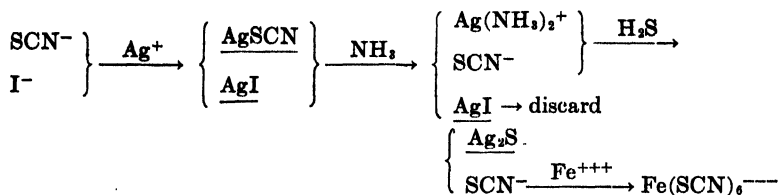


Complex Anions.—With certain cations, particularly Fe^{+++} and Co^{++} , SCN^- forms complex anions, as $\text{Fe}(\text{SCN})_6^{--}$ (blood red) and $\text{Co}(\text{SCN})_4^{--}$ (blue) (*cf.* pages 258, 261). The acids corresponding to these anions are soluble in organic solvents, such as ether and the alcohols.

Oxidation.—The SCN^- ion is decomposed by HNO_3 , forming colored solutions, usually red. These solutions are decolorized by boiling. Upon intensive oxidation, the products seem to be SO_4^{--} and HCN .



Detection.—The usual test for SCN^- is the formation of a red color with FeCl_3 solution. I^- ions interfere by being oxidized by the Fe^{+++} to red-brown I_2 . The I^- , if present, must be removed by adding excess Ag^+ and extracting the AgSCN from the AgI-AgSCN mixture by NH_4OH . The Ag^+ in the filtrate is then removed by H_2S . The solution is acidified with HCl , and the test for SCN^- is made by adding FeCl_3 in the usual way. The separation may be thus outlined:



FERROCYANIDE

Ferrocyanides were formerly called *yellow prussiates*. The formula of the anion is $\text{Fe}(\text{CN})_6^{---}$, in which the iron is bivalent.

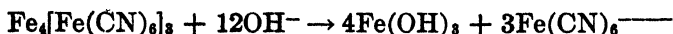
The Acid.—Ferrocyanic acid, $\text{H}_4\text{Fe}(\text{CN})_6$, is a white solid, readily soluble in water. Its aqueous solution is strongly acidic, so that solutions of its salts show little tendency to hydrolyze. Solutions of the acid are rather unstable, turning blue in contact with the air. Evidently, oxidation occurs, probably forming a little Fe^{+++} , which combines with excess $\text{Fe}(\text{CN})_6^{---}$, forming Prussian blue.

Solubilities.—The simple ferrocyanides of Group V are soluble in water, and those of Group IV are fairly soluble. Others are insoluble, or nearly so. There are a number of complex ferrocyanides of varying degrees of solubility.

Alkaline Ferrocyanides.—Potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, was formerly the source material for other ferrocyanides. Since the World War, it has been almost entirely replaced by the cheaper sodium ferrocyanide. The latter salt is made by reacting sodium cyanide with ferrous salts: $6\text{CN}^- + \text{Fe}^{++} \rightarrow \text{Fe}(\text{CN})_6^{---}$. Some $\text{Na}_4\text{Fe}(\text{CN})_6$ is obtained from the scrubbers used in purifying coal gas (the Buebe process).

Silver Ferrocyanide.— Ag^+ and $\text{Fe}(\text{CN})_6^{---}$ ions combine, forming $\text{Ag}_4\text{Fe}(\text{CN})_6$, white and insoluble in dilute HNO_3 and in NH_4OH , but soluble in CN^- solutions.

Ferric Ferrocyanide.— $\text{Fe}(\text{CN})_6^{---}$ ions combine with Fe^{+++} ions, forming Prussian blue, $\text{K}_4[\text{Fe}(\text{CN})_6]_3$. This salt is insoluble in water and dilute acids but is decomposed upon warming with NaOH or KOH solutions.



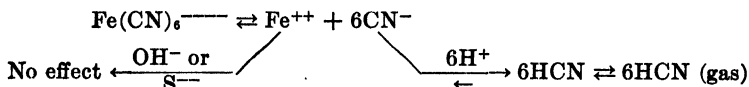
Ferrous Ferrocyanide.—This salt, which has the formula $\text{Fe}_2\text{Fe}(\text{CN})_6$, is really pure white in color. Usually the product has a blue color, owing to the presence of traces of Fe^{+++} in the

Fe^{++} solution, or to traces of $\text{Fe}(\text{CN})_6^{--}$ in the $\text{Fe}(\text{CN})_6^{--}$ solution. The blue color then is due to a small amount of Prussian or Turnbull's blue.

Cupric Ferrocyanide.—See page 203.

Zinc Ferrocyanide.—See page 249.

Stability of the Ferrocyanide Group.—The ferrocyanide ion would be expected to dissociate more or less into Fe^{++} and CN^- ions: $\text{Fe}(\text{CN})_6^{--} \rightleftharpoons \text{Fe}^{++} + 6\text{CN}^-$. This dissociation is extremely slight—so slight that the concentration of Fe^{++} is too small to give a precipitate with either OH^- or S^{--} ions; and the concentration of CN^- is too small for ferrocyanides to be poisonous. Although the equilibrium cannot be displaced noticeably by bases, it can be displaced by boiling with acids.



The greater efficiency of H^+ ions over OH^- ions is due to three reasons: (1) HCN , although more soluble than $\text{Fe}(\text{OH})_2$, is ionized to a much smaller extent. (2) HCN is volatile. (3) The concentration of CN^- ions is six times that of the Fe^{++} ions, giving it a sixfold advantage.

Oxidation to Ferricyanide.—Strong oxidizing agents oxidize $\text{Fe}(\text{CN})_6^{--}$ to $\text{Fe}(\text{CN})_6^{-}$ —e.g., $\text{Cr}_2\text{O}_7^{--}$, MnO_4^- , HNO_3 , Cl_2 , etc.

Ignition.—Upon ignition, most ferrocyanides are decomposed, giving a complex mixture of products.

Detection.—The $\text{Fe}(\text{CN})_6^{--}$ ion is generally detected by the formation of Prussian blue upon the addition of FeCl_3 .

FERRICYANIDE

The ferricyanides were formerly called *red prussiates*. The formula of the anion is $\text{Fe}(\text{CN})_6^{-}$, in which the iron is trivalent.

The Acid.—Ferricyanic acid, $\text{H}_3\text{Fe}(\text{CN})_6$, is a brown solid, easily soluble in water, giving a strongly acid solution. In the free state, $\text{H}_3\text{Fe}(\text{CN})_6$ is unstable, decomposing slowly in the cold and rapidly in the hot, evolving HCN : $\text{H}_3\text{Fe}(\text{CN})_6 \rightarrow 3\text{HCN} + \text{Fe}(\text{CN})_3$. The residue turns blue slowly, suggesting reduction either of $\text{Fe}(\text{CN})_6^{-}$ to $\text{Fe}(\text{CN})_6^{--}$ or of Fe^{+++} to Fe^{++} , forming either Prussian or Turnbull's blue.

Solubilities.—The ferricyanides of Cation Groups IV and V and of Hg^{++} , Sn^{++++} , Fe^{+++} , and Cr^{+++} are soluble in water; the others are insoluble.

Alkaline Ferricyanides.—Until recently, the most important salt has been potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, formed by oxidizing the ferrocyanide with Cl_2 : $2\text{Fe}(\text{CN})_6^{--} + \text{Cl}_2 \rightarrow 2\text{Fe}(\text{CN})_6^{-} + 2\text{Cl}^-$. This salt has now been replaced industrially by the sodium salt, which is the source of all other ferricyanides. It is used in the textile industry and in making certain dyestuffs.

Ignition.—Ferricyanides are generally decomposed by heating, giving a complex mixture of products (*cf.* $\text{Fe}(\text{CN})_6^{--}$).

Silver Ferricyanide.— Ag^+ ions precipitate $\text{Fe}(\text{CN})_6^{--}$ as orange $\text{Ag}_3\text{Fe}(\text{CN})_6$, insoluble in dilute HNO_3 . It differs from the ferrocyanide, $\text{Ag}_4\text{Fe}(\text{CN})_6$, in being soluble in NH_4OH .

Ferrous Ferricyanide.— Fe^{++} salts combine with $\text{Fe}(\text{CN})_6^{--}$ ions, forming ferrous ferricyanide, $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$, commonly known as Turnbull's blue.

Ferric Ferricyanide.— $\text{Fe}[\text{Fe}(\text{CN})_6]$ is soluble, forming a brown solution. A mixture of ferric citrate and $\text{K}_3\text{Fe}(\text{CN})_6$ is decomposed by light, giving a blue precipitate. This is the principle of blueprint paper.

Reduction.—Alkaline solutions of $\text{Fe}(\text{CN})_6^{--}$ are good oxidizing agents and are readily reduced to ferrocyanides: *e.g.*, $2\text{Fe}(\text{CN})_6^{--} + \text{SO}_3^{--} + 2\text{OH}^- \rightarrow 2\text{Fe}(\text{CN})_6^{-} + \text{SO}_4^{--} + \text{H}_2\text{O}$.

Detection.—The $\text{Fe}(\text{CN})_6^{--}$ ion is detected by the formation of a precipitate of Turnbull's blue with Fe^{++} ions.

SULFIDE

There are two sulfide ions—the normal sulfide S^{--} , and the hydrogen sulfide SH^- . As will be seen below, the S^{--} ion, on account of its hydrolytic reaction with water, is present only in very small concentrations. These ions are in ready equilibrium with each other, so that they give the same reactions.

The Acid.—The acid corresponding to the sulfide ions is hydrosulfuric acid, more commonly called *hydrogen sulfide*.

Hydrogen sulfide is a colorless gas, with an offensive odor, liquefying at -62.8° to a colorless liquid. Notwithstanding this

low boiling point, H_2S can be liquefied at ordinary temperatures by pressure alone and as such is shipped in steel cylinders as an article of commerce. The gas is poisonous, and a number of fatalities have been caused by breathing moderate concentrations. It is fairly soluble in water, 1 l. dissolving about 2.5 l. (slightly more than $\frac{1}{10}$ mole) of H_2S . Hydrogen sulfide is rather difficult to expel from solution, boiling for 1 or 2 min. being necessary in ordinary cases.

Hydrogen sulfide is generally prepared by the action of non-oxidizing acids on sulfides— FeS , usually.

The following ionization constants are generally accepted:

$$\text{For the primary ionization, } K_1 = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = 0.91 \times 10^{-7}$$

$$\text{For the secondary ionization, } K_2 = \frac{[\text{H}^+][\text{S}^{--}]}{[\text{HS}^-]} = 1.2 \times 10^{-15}$$

Multiplying,

$$K_{\text{over-all ionization}} = \frac{[\text{H}^+]^2[\text{S}^{--}]}{[\text{H}_2\text{S}]} = 1.1 \times 10^{-22}$$

Since the solubility of H_2S at room temperature is approximately 0.1 molar, the expression may be further simplified, thus:

$$K = [\text{H}^+]^2[\text{S}^{--}] = 1.1 \times 10^{-23}$$

This expression has the form of a solubility product (see page 89). It differs from a true ion product in that it is not a definite constant but varies with the concentration of the H_2S in the gaseous space above the solution.

From the above ionization constants, the concentrations of H^+ and SH^- ions in a saturated aqueous solution of H_2S may be calculated to be something less than 1×10^{-4} mole per liter, while that of the S^{--} ion is only 1.2×10^{-15} . In an effort to make this low concentration more concrete and real, it might be said that it would take 200 cubic miles of saturated H_2S to contain a single gram ion (32 g.) of ionic sulfur. In other words, if Lake Michigan were saturated with H_2S , it would contain only about 15 gram ions (or 480 g.) of S^{--} ions. On the other hand, assuming that there are 6×10^{23} molecules in a mole, the picture does not look so extreme and incredible. A liter of saturated H_2S should

contain $(1.2 \times 10^{-15}) \times (6 \times 10^{23})$, or 7.2×10^8 actual S^{--} ions; and the average distance between two neighboring ions should be only slightly more than 0.1 mm.

Owing to the low ionization (or high stability) of the HS^- ion, sulfides are highly hydrolyzed. For example, it has been calculated that molar Na_2S is 90 per cent hydrolyzed. That is, the concentrations of the anions in M Na_2S are: SH^- , 0.9 molar; OH^- , 0.9 molar; and S^{--} , 0.1 molar. For more dilute solutions, the degree of hydrolysis will be even greater, so that equimolecular mixtures of $NaOH$ and $NaSH$ are approximated.

Solubilities.—The only sulfides soluble in water are Na_2S , K_2S , and $(NH_4)_2S$. The sulfides of Group IV are only slightly soluble. However, they slowly pass into solution upon standing, owing to hydrolysis; *e.g.*, $2CaS + 2HOH \rightarrow Ca(OH)_2 + Ca(SH)_2$. These alkaline earth sulfides are readily soluble in NH_4^+ solutions, and for this reason are not precipitated in Cation Group III. The remaining sulfides may be divided into two groups, depending on whether or not they can be precipitated in the presence of dilute HCl . This, it will be recalled, is the basis for separating Cation Group III from Cation Group II.

Sodium Sulfide.—The usual source of the S^{--} ion is Na_2S , formed by heating Na_2SO_4 with coal at high temperatures: $Na_2SO_4 + 4C \rightarrow Na_2S + 4CO$. As stated above, its solutions are highly hydrolyzed into SH^- and OH^- and contain relatively few S^{--} ions.

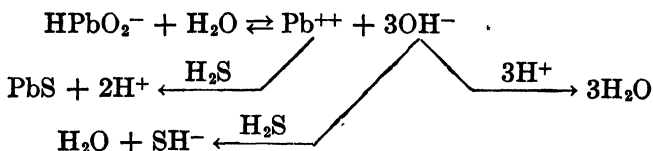
Silver Sulfide.—This salt is thrown down as a black precipitate when H_2S is introduced into an Ag^+ solution: $2Ag^+ + H_2S \rightarrow Ag_2S + 2H^+$. Ag_2S is insoluble in cold HNO_3 but dissolves upon warming. Its solubility in water is estimated at 3.4×10^{-17} mole per liter, giving too low a concentration of Ag^+ ions for it to react with NH_3 or $S_2O_3^{--}$ solutions. It is slightly decomposed by excess CN^- solution.

Many metals are tarnished by contact with materials containing sulfur. Silver, for example, will remove sulfur from many materials, forming black Ag_2S .

Barium Sulfide.—Owing to hydrolytic effects, Ba^{++} and S^{--} ions do not precipitate the slightly soluble BaS .

Lead Sulfide.— H_2S precipitates PbS from Pb^{++} solutions where the H^+ concentration does not exceed about 0.25 molar.

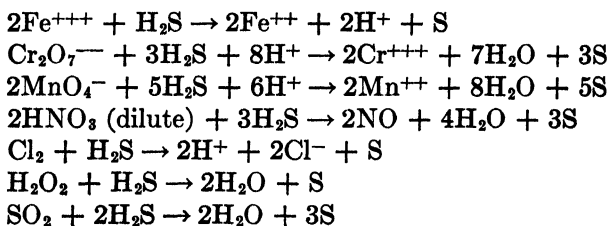
It also precipitates PbS from alkaline solutions, where the lead is present as the HPbO_2^- anion. This is another case of cooperative displacement.



The concentration of Pb^{++} in this system is very low—too low for PbS to form without assistance. This assistance comes in the form of a removal of the OH^- ions by (1) H_2S forming SH^- , and (2) the H^+ ions formed in the precipitation of PbS from Pb^{++} .

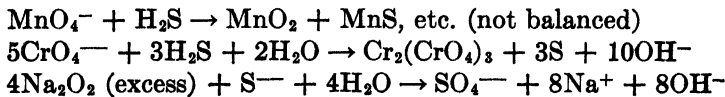
Reducing Action.—Sulfides, in both acid and alkaline solution, are active reducing agents. For example,

In acid medium:



It will be noted that, in acid medium, the normal oxidation products of H_2S are H_2O and S .

In alkaline medium:



The question, Which is the more powerful reducing agent, H_2S or S^{2-} ? has been extensively studied. It is not easy to answer, for change in the medium changes the oxidation-reduction potential of both reactants. In general, the best reducing effects are had in acid solution, suggesting that H_2S molecules are better than S^{2-} ions.

Detection.—The procedure depends largely upon the form of the material to be tested.

efficient in cleaning the coin from grease and other materials that might hinder good contact.

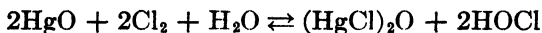
HYPOCHLORITE

Hypochlorites are constituents of the reagents used in the textile industry in bleaching cotton goods. They are also used as deodorants and disinfectants; *e.g.*, Dakin's solution is a 0.45 per cent solution of sodium hypochlorite, NaOCl.

Formation.—Chlorine is hydrolyzed by water, forming a mixture of hydrochloric and hypochlorous acids, thus: $\text{Cl}_2 + \text{HOH} \rightleftharpoons \text{H}^+ + \text{Cl}^- + \text{HOCl}$. In the presence of bases, these acids are neutralized, giving a mixture of chloride and hypochlorite, thus: $\text{Cl}_2 + 2\text{OH}^- \rightarrow \text{Cl}^- + \text{OCl}^- + \text{H}_2\text{O}$.

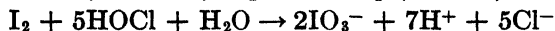
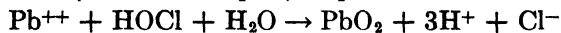
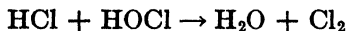
Industrially, hypochlorites are prepared by (1) the action of Cl_2 on bases, as $\text{Ca}(\text{OH})_2 + \text{Cl}_2 \rightarrow \text{CaOCl}_2$ (bleaching powder) + H_2O ; and (2) the electrolysis of alkaline chlorides, as $\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{NaOCl}$ (at anode) + H_2 (at cathode).

The Acid.—Hypochlorous acid, HOCl, is unknown except in solution. It is a very weak acid, displaced from its salts by acids as weak as H_2CO_3 . Its ionization constant is 3.7×10^{-8} . A dilute solution may be prepared by shaking chlorine water with yellow mercuric oxide.

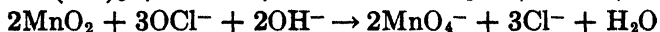
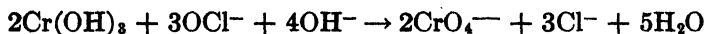


Hypochlorous acid tends to decompose with the formation of oxygen, thus: $2\text{HOCl} \rightarrow 2\text{H}^+ + 2\text{Cl}^- + \text{O}_2$. This reaction is catalyzed by light.

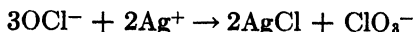
Oxidizing Action.—Hypochlorites are powerful oxidizing agents. In acid solution, they effect such oxidations as the following:



In alkaline solution, they are even stronger oxidizing agents than Na_2O_2 .



Reaction with Silver Ions.—A curious reaction takes place when OCl^- ions are mixed with Ag^+ .



That is, one OCl^- is oxidized to ClO_3^- , while two are reduced to Cl^- . This reaction is responsible for OCl^- being placed in Anion Group I, although it is only partially precipitated.

Reactions with Mercury.—The reactions when hypochlorites are shaken with mercury vary with conditions. In the presence of strong acids, white mercurous chloride, Hg_2Cl_2 , is formed (owing to free Cl_2). In solutions of HOCl , a brown precipitate of basic mercuric chloride is formed: $2\text{Hg} + 2\text{HOCl} \rightarrow (\text{HgCl})_2\text{O} + \text{H}_2\text{O}$. This precipitate is soluble in HCl . In alkaline solution, yellow HgO is formed: $\text{Hg} + \text{OCl}^- \rightarrow \text{HgO} + \text{Cl}^-$. Other Cl -containing anions have no effect.

Detection.—The principal test for the OCl^- ion is the formation of a yellow precipitate, soluble in HCl , when alkaline solutions are shaken with metallic mercury. A supporting test is the decolorization of indigo solution.

SPECIAL ANALYTICAL PROCEDURES

The tests for the ions of Anion Group I are subject to a number of interferences, which necessitate preliminary separations. For example, the usual test for Cl^- is the formation of white AgCl —a reaction with which every other member of Anion Group I interferes.

Chloride in the Presence of Bromide.—Probably the most reliable method for detecting Cl^- in the presence of Br^- consists in precipitating the two ions as AgCl and AgBr . The mixture is extracted with a NaOH solution sufficiently dilute so that the amount of AgBr extracted is negligible. The AgCl is much more soluble in NaOH , and the Cl^- in the extract is detected in the usual way. The concentration of the NaOH used is 0.1 per cent. It should be noted that this procedure does not involve a separation of Cl^- and Br^- .

Chlorine in the Presence of Thiocyanate.—The solution is made slightly alkaline with Na_2CO_3 and evaporated to dryness. A little $\text{Mn}(\text{NO}_3)_2$ is added and the residue ignited until it is black throughout. The MnO_2 thus formed destroys the SCN group

without affecting the chloride. The residue is extracted with dilute HNO_3 , and the extract tested for Cl^- by AgNO_3 in the usual way.

Bromide in the Presence of Iodide.—The I^- ion interferes with the Ag^+ test for Br^- by forming yellow AgI and with the displacement-by- Cl_2 test by forming I_2 , which gives a purple solution in CCl_4 . The I^- ion may be removed without loss of Br^- by oxidation with NaNO_2 and dilute H_2SO_4 followed by extraction of the free I_2 by CCl_4 .

Removal of Cyanide, Ferrocyanide, Ferricyanide, and Sulfide. These ions interfere with the test for Cl^- by giving precipitates with AgNO_3 and with the tests for Br^- and I^- by reacting with the Cl_2 used in displacing the halogens. These interfering ions are removed by adding a slight excess of $\text{Co}(\text{NO}_3)_2$ to the neutral solution and filtering out the insoluble Co^{++} salts.

Ferrocyanide and Ferricyanide in the Presence of Each Other. These anions can be detected in the presence of each other by appropriate reagents. However, they are usually present together; for their solutions are unstable, and each is formed as a decomposition product of the other.

Sulfides Insoluble in Acids.—The S^- in sulfides insoluble in HCl is liberated in the form of H_2S by the combined action of Zn and HCl . SCN^- , SO_3^- , and S_2O_3^- also evolve H_2S under this treatment and must be removed by washing with water or dilute HCl before the zinc is added.

Interference by Thiosulfate.—The S_2O_3^- ion interferes with the Ag^+ reaction in Anion Group I by (1) dissolving certain of the precipitates, (2) forming a precipitate of sulfur upon acidification, (3) forming $\text{Ag}_2\text{S}_2\text{O}_3$, which hydrolyzes into Ag_2S , giving a false test for S^- , and (4) under certain circumstances converting CN^- into SCN^- . It also interferes with the Fe^{+++} test for SCN^- by converting Fe^{+++} to Fe^{++} . If S_2O_3^- is present, it should be destroyed by acidification or oxidation before adding Ag^+ to the solution.

Exercises

1. Write equations for the oxidation of HCl by MnO_2 , HClO_2 , and NaBiO_3 .
2. If AgCl were absolutely insoluble in water, could it still be soluble in NH_4OH ?

3. Show mathematically that the solubility of AgCl in NH_4OH varies as the square of the concentration of the NH_3 , while its solubility in NaOH varies as the first power of the OH^- concentration.

4. Why will KCN solution dissolve AgCl but not Ag_2S ?

5. Which complex, $\text{Ag}(\text{NH}_3)_2^+$ or AgS_2O_3^- , ionizes the more? Cite reactions to support your opinion.

6. Judging from their reactions with HCl , HBr , and HI , arrange concentrated H_2SO_4 , HNO_3 , and $\text{MnO}_2 + \text{H}^+$ in the order of their oxidizing strength.

7. Name the members of Anion Group I that are oxidized by Cl_2 solution.

8. Suppose HCN were a strong acid. Could it be easily displaced by bubbling a stream of CO_2 through the solution?

9. Why do solutions containing S^{--} and CN^- generally give a test for SCN^- ?

10. HBrO_3 seems to be a stronger oxidizing agent than HNO_3 . Complete and balance the following equation: $\text{SCN}^- + \text{HBrO}_3 \rightarrow \dots$

11. How would you expect the halogenoid ions to react with Pb^{++} ?

12. What members of Anion Group I will not decolorize a cold, very dilute solution of KMnO_4 that has been acidified with H_2SO_4 ?

13. How many cubic centimeters of $0.05\text{ }M\text{ } \text{Cl}_2$ would be required to displace the iodine and bromine from a solution containing 3 cc. of $0.4\text{ }M\text{ } \text{KBr}$ and 2 cc. of $0.3\text{ }M\text{ } \text{KI}$?

14. What weight of BaCrO_4 would be formed (theoretically) in the CrO_2Cl_2 test on 0.585 g. of NaCl ?

15. There is added 2 cc. of $6\text{ }M\text{ } \text{HCl}$ to 10 cc. of $0.3\text{ }M\text{ } \text{AgNO}_3$. What volume of $6\text{ }M\text{ } \text{NH}_4\text{OH}$ must be added to the mixture to dissolve the AgCl precipitate?

16. What volume of $0.3\text{ }M\text{ } \text{AgNO}_3$ would be required to precipitate the Br^- as AgBr in a solution containing 4 cc. of $0.3\text{ }M\text{ } \text{KBr}$ and 3 cc. of $0.4\text{ }M\text{ } \text{NaCN}$?

17. Are solutions of $\text{Fe}(\text{CN})_6^{--}$ and $\text{Fe}(\text{CN})_6^{---}$ stable? What would you expect to find in a solution that contains both of these ions and that has stood for some time?

18. Refer to the Solubility Table, and suggest two cations other than Fe^{++} and Fe^{+++} that might be used to test for $\text{Fe}(\text{CN})_6^{--}$ and $\text{Fe}(\text{CN})_6^{---}$ in the presence of each other.

19. Give reagents and products in the following separations (see solubility tables): (a) Cl^- and I^- , (b) CN^- and $\text{Fe}(\text{CN})_6^{--}$, (c) $\text{Fe}(\text{CN})_6^{--}$ and $\text{Fe}(\text{CN})_6^{---}$, (d) free S and As_2S_3 , (e) $\text{Fe}(\text{SCN})_3$ and $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$.

20. Identify the following anions of Group I:

(a) An anion that gives with AgNO_3 a yellowish precipitate, insoluble in HNO_3 , but easily soluble in NH_4OH .

(b) An anion that gives with AgNO_3 a white precipitate, insoluble in HNO_3 , and with $\text{Co}(\text{NO}_3)_2$ a bluish precipitate, insoluble in dilute HCl .

(c) An anion that gives with FeCl_3 a reddish color but with AgNO_3 a yellow precipitate, insoluble in NH_4OH .

(d) An anion that gives a red precipitate with FeCl_3 but, after evaporation with $(\text{NH}_4)_2\text{S}_x$, a red solution with $\text{FeCl}_3 + \text{HCl}$.

21. A mixture of Group I anions gives, upon warming with a few drops of FeSO_4 solution and an excess of NaOH , a black precipitate, easily soluble in dilute HCl . After filtering, the yellow filtrate was acidified with HCl and FeCl_3 added, giving a deep blue color. What anions are indicated?

22. A mixture of Group I anions gave with AgNO_3 a black precipitate; with $\text{Co}(\text{NO}_3)_2$, a bluish black precipitate, insoluble in HCl ; with Cl_2 , a reddish solution containing a white precipitate. The reddish solution gave a red extract with CCl_4 , and the remaining portion gave a blue precipitate with FeSO_4 . What anions are indicated?

CHAPTER XXI

ANION GROUP II

This group consists of those anions whose Ag^+ salts are slightly soluble in water and easily soluble in dilute HNO_3 and whose Ba^{++} salts are soluble in water. The most important members of the group are as follows:

Acetate, $\text{C}_2\text{H}_3\text{O}_2^-$	[Cyanate, OCN^-]
Nitrite, NO_2^-	[Hypophosphite, H_2PO_2^-]
Hydroxyl, OH^-	
Peroxide, O_2^{--}	

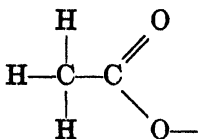
As usual, the brackets denote members of less importance.

Owing to the appreciable solubility of the acetate and nitrite of silver in water, precipitation may not occur when Ag^+ ions are added to dilute solutions of $\text{C}_2\text{H}_3\text{O}_2^-$ and NO_2^- ions. For this reason, these ions are also included in Anion Group IV. In general, tests for these ions should be made, even when the test for Anion Group II is negative.

ACETATE

There are a few anions of organic origin whose occurrence is so general that they are included in courses in inorganic analysis. Besides the acetate, the most common of these are oxalate and tartrate. Strictly speaking, carbonate and the cyanide anions are also organic compounds, though not of organic origin.

The Formula.—The formula for the acetate ion is written in various ways. The empirical formula, showing composition only is $\text{C}_2\text{H}_3\text{O}_2^-$. The structural formula



shows the linkage between the atoms and is used by organic

chemists. The abbreviation Ac^- is very frequently used in notes, equations, and calculations.¹

The Acid.—Pure (glacial) acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, is a colorless liquid, boiling at 118° . It is prepared: (1) by oxidizing ethyl alcohol by the air, using "mother of vinegar" (*mycoderma aceti*) as a catalyst; $\text{C}_2\text{H}_5\text{OH} + \text{O}_2 \rightarrow \text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O}$; (2) by distilling acetates with high-boiling acids, such as concentrated H_2SO_4 or H_3PO_4 ; e.g., $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HC}_2\text{H}_3\text{O}_2 + \text{CaSO}_4$.

Complex Formation.—The $\text{C}_2\text{H}_3\text{O}_2^-$ ion forms with certain cations very stable complexes, which fail to show some of the usual properties of cations. For example, PbSO_4 cannot be precipitated from a Pb^{++} solution to which an excess of $\text{C}_2\text{H}_3\text{O}_2^-$ ions has been added. The complex is usually considered to be the molecule $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. However, certain lines of evidence point to the formation of complex anions of the type $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_3^-$. This complex formation is characteristic of the ion $\text{C}_2\text{H}_3\text{O}_2^-$, and not of molecular $\text{HC}_2\text{H}_3\text{O}_2$. To illustrate: PbSO_4 dissolves only slightly in $\text{HC}_2\text{H}_3\text{O}_2$ solutions.

Oxidizability.—While $\text{HC}_2\text{H}_3\text{O}_2$ in the pure form burns readily, forming CO_2 and H_2O , its solutions are extremely resistant to oxidation. Only the very strongest oxidizing agents affect it; e.g., the persulfate ion $\text{S}_2\text{O}_8^{--}$ oxidizes it slowly. It is equally resistant to reducing agents. When fused with strong oxidizing agents, acetates are converted into carbonates or oxides with the evolution of CO_2 and H_2O .

Decomposition by Heat.—Acetates, when heated in the dry state under nonoxidizing conditions, undergo decomposition. Inflammable gases are given off, leaving a residue of carbonate or oxide. Charring may occur, but to a much less extent than with tartrates. The decomposition of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ is exceptional: $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 + \text{heat} \rightarrow \text{CH}_3\text{CONH}_2$ (acetamide) + H_2O .

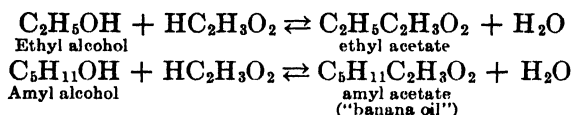
Ferric Acetate.—In neutral medium, Fe^{+++} and $\text{C}_2\text{H}_3\text{O}_2^-$ ions form a dark red solution. Upon heating, basic ferric acetate, $\text{Fe}(\text{OH})_2\text{C}_2\text{H}_3\text{O}_2$, is precipitated (see page 258). Iodide, thiocyanate, and a few other ions interfere with this reaction.

Silver Acetate.—In fairly concentrated solutions, Ag^+ and $\text{C}_2\text{H}_3\text{O}_2^-$ ions form white crystals of $\text{AgC}_2\text{H}_3\text{O}_2$. This salt is

¹ *Chemical Abstracts*, the abstract journal of the American Chemical Society, uses "Ac" as a symbol for the acetyl group, CH_3CO —. It therefore uses "OAc—" as the formula for the acetate ion.

appreciably soluble in water—about 0.066 mole per liter. This solubility, frequently increased by the presence of uncommon ions, is often sufficient to prevent the precipitation of the salt.

Acetate Esters.—When a mixture of $\text{HC}_2\text{H}_3\text{O}_2$ and an alcohol is warmed in the presence of a dehydrating agent—*e.g.*, concentrated H_2SO_4 —organic salts (“esters”) are formed. For example:



The concentrated H_2SO_4 favors the forward reactions by combining with the water formed. These esters have odors that are more or less distinctive, though they may be obscured by other odors.

Detection.—The detection of the $\text{C}_2\text{H}_3\text{O}_2^-$ ion in the presence of other substances is difficult for the following reasons: (1) There are no acetates of sufficient insolubility to form the basis of a precipitation test. (2) The ion is very stable toward oxidizing and reducing agents, giving no products that may be used for its identification (*cf.* NO_3^- , page 390). All that can be done is to convert the ion into the free acid, or one of its esters, and identify these by their odors.

1. *Formation of Free Acetic Acid.*—If an acetate is warmed with concentrated H_2SO_4 , $\text{HC}_2\text{H}_3\text{O}_2$ is given off as a vapor and may be recognized by its sharp biting odor. This test may be masked by the presence of other anions that give off gases with strong odors. For example, sulfites and thiosulfates give off SO_2 , sulfides give H_2S , nitrites NO and NO_2 , iodides I_2 , and chlorides and nitrates may give enough of their acids to obscure the odor of $\text{HC}_2\text{H}_3\text{O}_2$. In such cases, the interfering anions must be removed— S^- and the halide ions by Ag_2SO_4 , SO_3^- and S_2O_3^- by KMnO_4 , and NO_2^- by urea, or by careful warming with dilute H_2SO_4 .

2. *Formation of Ethyl Acetate.*—The most frequent test for the $\text{C}_2\text{H}_3\text{O}_2^-$ ion is the formation of ethyl acetate, $\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$, when an acetate is warmed with $\text{C}_2\text{H}_5\text{OH}$ in the presence of concentrated H_2SO_4 . Amyl acetate, $\text{C}_5\text{H}_{11}\text{C}_2\text{H}_3\text{O}_2$, has a more conspicuous odor than ethyl acetate; however, the heavy odor of the

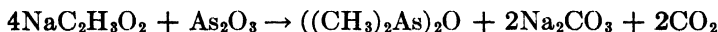
excess C_2H_5OH is apt to obscure the test. Ethyl alcohol, on the other hand, is practically odorless.

Certain anions interfere with the ethyl acetate test, particularly NO_2^- and Br^- . These form the esters $C_2H_5NO_2$ (ethyl nitrite) and C_2H_5Br (ethyl bromide), which have about the same volatility as $C_2H_5C_2H_3O_2$.

Another interference is found in the fact that C_2H_5OH and H_2SO_4 may react, forming products with decided odors—*e.g.*, ethyl ether, $(C_2H_5)_2O$, or even acetaldehyde, CH_3CHO .

The best way to overcome these interferences is to carry out, along with the test on the unknown, a *control test* and a *blank test*. In the control test, an acetate, C_2H_5OH , and H_2SO_4 are used; in the blank test, C_2H_5OH and H_2SO_4 . By comparing the odor from the unknown with these known odors, the reliability of the test may be considerably increased.

3. *Cacodylic Oxide*.—When an alkaline acetate is ignited with As_2O_3 , cacodylic oxide is formed as a foul and very poisonous gas; *e.g.*,



This test is too dangerous for ordinary use.

4. *Basic Lanthanum Acetate*.—When a solution containing $C_2H_3O_2^-$ and La^{+++} ions is made slightly alkaline with NH_4OH , a basic acetate is formed which has the property of adsorbing free iodine, giving a blue color. The procedure is as follows:

To the unknown solution is added about 0.5 cc. each of 5 per cent $La(NO_3)_3$ and a KI solution of I_2 . The mixture is then made slightly alkaline with NH_4OH and slowly heated to the boiling point. A blue color indicates $C_2H_3O_2^-$.

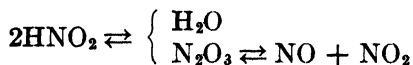
This test is very sensitive, but its usefulness is limited by interferences. Certain other organic anions besides $C_2H_3O_2^-$ give positive tests, while the anions of Groups III and V prevent the test by forming insoluble La^{+++} precipitates.

NITRITE

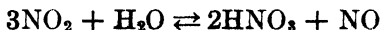
The nitrite ion, NO_2^- , is univalent and colorless. Its alkaline salts are industrially important in the preparation of dyestuffs.

The Acid.—On account of its instability, pure nitrous acid is not known. Upon concentrating its solutions, it dissociates into

water and nitrous anhydride, N_2O_3 ; and the latter dissociates into a mixture of NO and NO_2 .



Some of this NO_2 reacts with water, forming nitric acid.

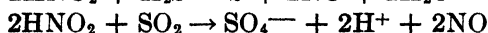
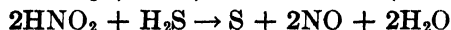
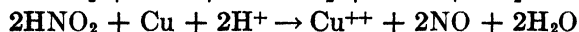
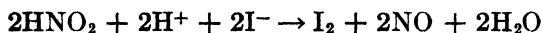


Consequently, a certain amount of HNO_3 is a normal impurity in HNO_2 solutions.

Nitrous acid is a fairly strong acid, with a dissociation constant of 4.5×10^{-4} .

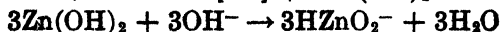
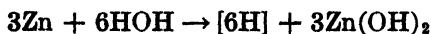
Solubilities.—All stable nitrites are soluble in water except $AgNO_2$, which is slightly soluble.

Oxidizing Action.—Nitrites in acid solution react vigorously with certain reducing agents; in neutral or alkaline medium, the oxidizing action is slight. The inference is that HNO_2 molecules are strong oxidizing agents, whereas the NO_2^- ion as such has little oxidizing power. The following are typical reactions:



Although HNO_2 is a weaker acid than HNO_3 , it is a speedier oxidizing agent. For example, M $NaNO_2$ + dilute H_2SO_4 will dissolve copper more rapidly than M HNO_3 . This seems to be due to the fact that HNO_3 is largely ionized into H^+ and NO_3^- ions and that the NO_3^- is not an oxidizing agent, or at best a feeble one. On the other hand, HNO_2 is mainly in the molecular form, which is an active oxidizing agent.

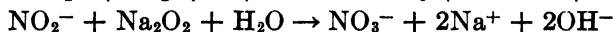
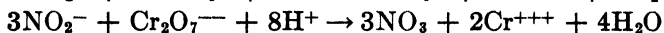
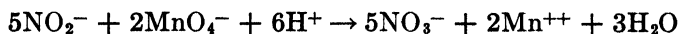
In alkaline medium, nitrites react only with the most powerful reducing agents. The most important reaction—and one that should not be forgotten—is the reduction of NO_2^- to NH_3 by zinc dust in the presence of $NaOH$. The zinc displaces the hydrogen from water, and the $NaOH$ favors the reaction by dissolving the $Zn(OH)_2$, which otherwise would act as a protective agent.



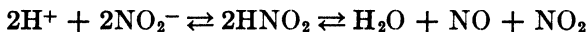
Adding,



Reducing Action.—Toward strong oxidizing agents, the NO_2^- ion behaves as a reducing agent, and is oxidized to NO_3^- ; *e.g.*,

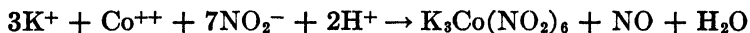


The dual behavior of nitrites, acting as both oxidizing and reducing agents, becomes intelligible when it is noted that HNO_2 molecules and NO_2 are oxidizing agents, whereas NO_2^- ions are reducing agents. As seen from the equilibrium



an increase in acidity shifts the equilibrium to the right, with the formation of the active oxidizing agents HNO_2 and NO_2 . Removal of H^+ ions (*e.g.*, by neutralization by bases) shifts the equilibrium to the left, forming NO_2^- , which is a weak reducing agent.

Detection.—Since there are no insoluble nitrites, the detection of the NO_2^- ion by precipitation is out of the question. The nearest approach to this form of test is the formation of potassium or ammonium cobaltinitrite, which are only sparingly soluble; *e.g.*,



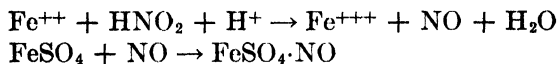
Equilibrium in this reaction may be shifted to the right by using high concentrations of K^+ and Co^{++} ions. The H^+ concentration must be kept low (dilute $\text{HC}_2\text{H}_3\text{O}_2$ is used) to prevent the withdrawal of NO_2^- ions as HNO_2 and its decomposition products. The mass law summarizes the situation very well. The speed of formation of $\text{K}_3\text{Co}(\text{NO}_2)_6$ may be expressed:

$$\bar{S} = k[\text{K}^+]^3[\text{Co}^{++}][\text{NO}_2^-]^7$$

The factor with the greatest effect is $[\text{NO}_2^-]$, for it functions as the seventh power. The equilibrium is much less affected by the K^+ concentration, which functions as the third power, and hardly at all by the Co^{++} concentration. That is, the reaction is most

sensitive in precipitating Co^{++} and least sensitive in precipitating NO_2^- .

Instead of precipitation reactions, the analyst must turn to decomposition reactions and make use of a decomposition product that gives a distinctive reaction. This is found in nitric oxide, NO , which forms a brown color with FeSO_4 solution. The Fe^{++} ion first reduces the HNO_2 to NO .



Owing to the weakness of HNO_2 , only a small acidity is needed to supply the H^+ ions required for the reaction; the free acid present in the reagent FeSO_4 is sufficient. Consequently, when FeSO_4 is added to a solution containing NO_2^- , the whole solution turns brown (*cf.* NO_3^- , page 390). The brown complex is decomposed by heat; therefore the reaction must be carried out in the cold.

One of the most sensitive of all the nitrite reactions is the oxidation of I^- ions to free I_2 . As little as 1 part of NO_2^- in 10,000,000 can be detected by this reaction. However, the test is not recommended, for it is not distinctive. Practically all oxidizing agents give it. The test is therefore worthless in the possible presence of other oxidizing agents.

Acid solutions of nitrites react with aromatic amines (derivatives of NH_2 and benzene-like compounds) to give highly colored products, called *diazo compounds*. For example, with diamino-benzoic acid an orange-red color is formed (the Griess reaction), which will detect 1 part of NO_2^- in 500,000. With sulfanilic acid and α -naphthylamine, a yellow color is obtained, giving a test of still higher sensitiveness. These reactions are used in the analysis of drinking water but are far too sensitive for general use.

Removal of Nitrite.—The FeSO_4 - NO reaction is also used in the detection of the nitrate ion NO_3^- . The NO_2^- ion therefore interferes, and the following procedures have been proposed for its removal. (1) When nitrites are gently ignited with NH_4^+ salts, the NH_4NO_2 formed decomposes as follows: $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$. (2) Urea, $(\text{NH}_2)_2\text{CO}$, is oxidized by HNO_2 at room temperature: $(\text{NH}_2)_2\text{CO} + 2\text{HNO}_2 \rightarrow 2\text{N}_2 +$

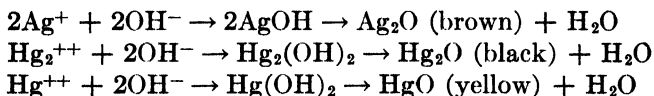
$\text{CO}_2 + 3\text{H}_2\text{O}$. Neither of these procedures is satisfactory, for some NO_3^- is always formed as a by-product.

HYDROXYL

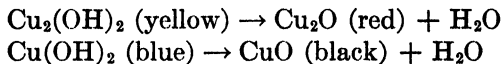
The OH^- ion is a typical anion and combines with cations, forming products that are saltlike in composition and behavior. There is no real need to distinguish between salts and bases. Bases might be defined as salts in which the anion is OH^- . They have a definite group of reactions, one of which is the formation with H^+ of a very weak acid, HOH . Other anions— CN^- , for example—approach this behavior.

Solubilities.—The hydroxides of Na^+ , K^+ , and NH_4^+ are easily soluble in water; the hydroxides of Ba^{++} , Sr^{++} , and Ca^{++} are moderately soluble; the hydroxides of the remaining metals are generally spoken of as insoluble, though it must be remembered that certain of these have appreciable solubilities. $\text{Mg}(\text{OH})_2$ and AgOH (*i.e.*, $\text{Ag}_2\text{O} + \text{H}_2\text{O}$) are soluble enough to give basic reactions with certain indicators.

Decomposition of Hydroxides.—The hydroxides of a few metals are so unstable that they decompose spontaneously into oxides and water.



The copper hydroxides are decomposed below 100° , *i.e.*, by boiling the solution in which they are suspended.



Most of the remaining hydroxides are dehydrated with more or less difficulty. $\text{Fe}(\text{OH})_3$ begins to lose water at 500° , and $\text{Si}(\text{OH})_4$ must be heated above 1000° to dehydrate it completely. NaOH and KOH cannot be dehydrated at all.

Tests.—There is no dearth of tests for OH^- ions. Any of the indicators used in acidimetry and alkalimetry may be used—*e.g.*, litmus (blue), phenolphthalein (red), methyl orange (yellow), etc.

However, a positive test with one of these reagents does not necessarily indicate that the original substance contained a

hydroxide or oxide. The OH^- ion may have come from the water, owing to hydrolysis of a salt. For example, Na_2CO_3 gives an alkaline reaction, owing to the decomposition of water by the CO_3^{--} ion: $\text{H}_2\text{O} + \text{CO}_3^{--} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$. If no anions other than OH^- can be found in a solution, the presence of an ionizing hydroxide or oxide is fairly certain. This inference, however, should be checked against the physical properties of the original substance. For example, before a calcium compound is reported as lime, the unknown should have the appearance and general behavior of either hydrated lime or quicklime. Hydroxides, in most cases, may be distinguished from oxides by heating in a dry test tube, whereupon a condensate of water will form on the colder walls of the tube. NaOH and KOH are exceptions, for they are not decomposed by heat. It should be remembered that hydrated salts and deliquescent substances give off water upon ignition.

There are cases where the expected hydrolysis may be lacking, owing to the presence of another salt that neutralizes the solution. To illustrate: Na_2CO_3 does not give an alkaline reaction in the presence of excess BaCl_2 , since the CO_3^{--} ion is tied up as precipitated BaCO_3 .

The presence of hydroxides or oxides in mixtures may be established quantitatively by the lack of equivalence of anions to cations. For example, a quantitative analysis of a Bi-Cl compound shows 80.24 per cent Bi and 13.61 per cent Cl. The remaining 6.15 per cent may be water of hydration, or hydroxyl, or oxygen. Dividing these percentages by the equivalent weights of the ions, we have $\text{Bi}:\text{Cl}::\frac{80.24}{69.67}:\frac{13.61}{35.46}$, or 3:1. That is, the anions are short by two equivalents. Inspection shows that this shortage may be made up by one O group, and that the compound is the basic chloride, BiOCl (bismuthyl chloride).

Ionization of Water.—Conductivity measurements indicate that water is 0.00001 per cent ionized at 25° . That is, the concentration of H^+ and OH^- ions is each 0.0000001 gram ion per liter. It is therefore a very weak electrolyte, and in most cases its ionization may be neglected. In other cases, particularly hydrolysis (see page 129), this ionization becomes very important.

The ionization constant may be calculated by substituting in the expression

$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = K_{\text{ionization}}$$

$[\text{H}^+] = [\text{OH}^-] = 0.0000001$; $[\text{H}_2\text{O}] = 1,000 \div 18 = 55.6$. The ionization constant is therefore 1.8×10^{-16} . A more useful expression is the ion product. For dilute solutions, $[\text{H}_2\text{O}]$ may be regarded as a constant ($= 55.6$); substituting, in the expression for the ionization constant,

$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{10^{-7} \times 10^{-7}}{55.6} = 1.8 \times 10^{-16}$$

or,

$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} = K_{\text{sol. prod.}}$$

This ionization of water increases with the temperature (see Table 7, page 129). This is unusual, for in most cases an increase in temperature represses ionization. This increase in the OH^- concentration from water is sometimes sufficient to make reactions proceed at high temperatures, while they go slowly or not at all at room temperature (see basic ferric acetate, page 258). For the same reason, hydrolysis is greater at high temperatures.

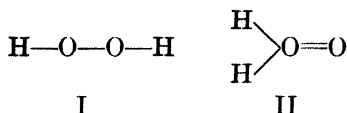
PEROXIDE

The alkaline peroxides, Na_2O_2 and K_2O_2 , are fairly soluble in cold water without decomposition, forming solutions that give a dark-gray precipitate with AgNO_3 solution, soluble in HNO_3 . It follows that the hypothetical peroxide ion, O_2^- , is a member of Anion Group II.

Hydrogen Peroxide.—Hydrogen peroxide is to be considered the parent acid of the O_2^- anion. As such, it is weak, ionizing feebly, thus: $\text{H}_2\text{O}_2 \rightleftharpoons 2\text{H}^+ + \text{O}_2^-$. In the presence of bases, the equilibrium is shifted to the right by the removal of H^+ ions, increasing the concentration of the O_2^- ions. For this reason, H_2O_2 in the presence of bases behaves like Na_2O_2 .

Hydrogen peroxide usually comes on the market as a 3 per cent solution. This concentration is sometimes called 10 *volume*, because 1 l. when treated with an oxidizing agent, such as HMnO_4 , will liberate 10 l. of oxygen. The reagent "perhydrol" is approximately a 30 per cent or "100-volume" solution.

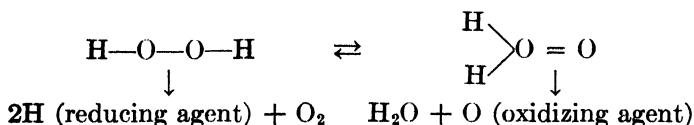
Constitution.—Two structures have been proposed for H_2O_2 .



Formula I is supported by the reactions of organic peroxides and certain physical properties. The evidence for formula II is that it gives a picture of how H_2O_2 , in its oxidation reactions, can give off one atom of oxygen and leave a molecule of water as a residue,

as follows: $\begin{array}{c} \text{H} \\ \diagup \\ \text{O}=\text{O} \\ \diagdown \\ \text{H} \end{array} \rightarrow \begin{array}{c} \text{H} \\ \diagup \\ \text{O} \\ \diagdown \\ \text{H} \end{array} + \text{O}$. Some writers like to think

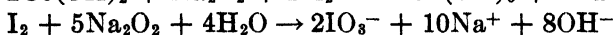
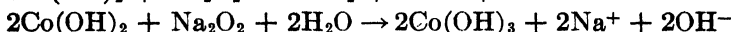
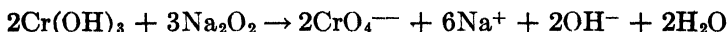
that both forms of H_2O_2 exist in equilibrium with each other.



Conclusive evidence to support this theory is not forthcoming.

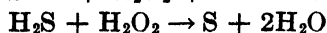
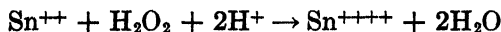
Oxidizing Action.—The oxidizing strength of peroxides varies with the acidity or alkalinity of the solution.

Alkaline Medium.—In alkaline solution, peroxides are strong oxidizing agents; *e.g.*,



The O_4^{--} ion is not so strong an oxidizing agent as OCl^- ; the latter will convert Ni^{++} into $\text{Ni}(\text{OH})_3$, but the former gives $\text{Ni}(\text{OH})_2$.

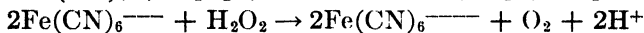
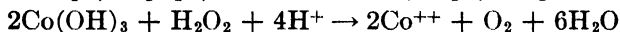
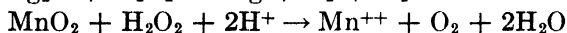
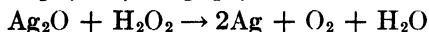
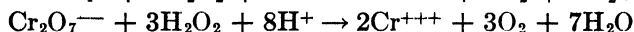
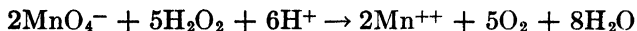
Acidic Medium.—In acid solution, peroxides are weak oxidizing agents, reacting only with very strong reducing agents; *e.g.*,



This difference in oxidizing strength may be explained by assuming that the oxidizing action is due to the O_2^{--} ion. The

action in acid solution is feeble, owing to the repression of the ionization of H_2O_2 by the excess H^+ ions.

Reducing Action.—In acidic medium, H_2O_2 has marked reducing properties, reacting with many of the stronger oxidizing agents.



The reducing action of H_2O_2 in acid solution seems to be due to the H_2O_2 molecules.

It should be noticed that whenever H_2O_2 acts as a reducing agent, O_2 is liberated; whenever it acts as an oxidizing agent, H_2O is formed.

Many students in their earlier courses in chemistry get the notion that O_2 is a strong oxidizing agent. Such is not the case, except at high temperatures. Many reducing agents will not react with gaseous oxygen at ordinary temperatures—*e.g.*, Mn^{++} , $\text{H}_2\text{C}_2\text{O}_4$, etc. In a similar way, hydrogen is not a reducing agent except at high temperatures. Strong oxidizing agents, like HMnO_4 and $\text{H}_2\text{Cr}_2\text{O}_7$, are not affected by bubbling hydrogen through them.

Pseudo Peroxides.— PbO_2 , MnO_2 , NiO_2 , etc., are sometimes called *peroxides*. The metals in these cases are probably quadrivalent, and for that reason they are better considered *dioxides*. They do not liberate H_2O_2 on acidification, as is the case with true peroxides.

Detection.—The following reactions are used in testing for “true” peroxides:

1. The formation of blue “perchromic acid” with a soluble chromate in the presence of H_2SO_4 and ether (see page 248) is the usual test.

2. With titanium sulfate, $\text{Ti}(\text{SO}_4)_2$, solution, peroxides form yellow pertitanic acid, H_2TiO_4 , or $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$. This is the most sensitive and trustworthy of the tests for peroxides.

3. Peroxides liberate I_2 from neutral I^- solutions. This test is sensitive, but it is not specific, for most oxidizing agents show this effect.

4. The bleaching of permanganate solutions is another reaction that is of doubtful value as a test, for many other reducing agents act similarly.

5. The reduction of $Ag(NH_3)_2^+$ to gray silver has been proposed, but the test is not so reliable as (1) and (2) in the foregoing paragraphs.

Peracids.—There are a number of acids whose salts undergo decomposition in solution, forming peroxides: *e.g.*, percarbonic acid, $H_2C_2O_6$; perboric acid, HBO_3 ; perchromic acid, H_3CrO_8 (?); pertitanic acid, H_2TiO_4 or H_4TiO_6 , etc. There is another group of acids that are considered “false” peracids, because they do not show this decomposition into peroxides. Examples are perchloric, periodic, permanganic, etc.

Since “true” peracids show all the reactions of peroxides, they are mentioned at this time.

SPECIAL ANALYTICAL PROCEDURES

Acetate in the Presence of Interferences.—The ethyl acetate test for $C_2H_3O_2^-$ may be improved by removing ions that tend to mask the ethereal odor. The ions of Anion Group I are removed by adding a slight excess of $AgNO_3$ and filtering while warm (to keep the $AgC_2H_3O_2$ in solution). If the solution is neutral or alkaline, the $AgNO_3$ will also remove the interfering anions of Group III— SO_3^- and $S_2O_3^{--}$, in particular. The addition of $KMnO_4$ will also remove the latter ions by oxidizing them to SO_4^{--} .

Nitrite in the Presence of Group I Anions.—Several of the anions of Group I interfere with the $FeSO_4$ test for NO_2^- . $Fe(CN)_6^{--}$ ions give a blue precipitate and S^{--} ions a black precipitate with the reagent, and $Fe(CN)_6^{--}$ ions give a blue color and SCN^- ions a red color with any Fe^{+++} ions that are usually present as an impurity. Consequently, these ions are removed, preferably by $AgNO_3$. In neutral solution, Group III anions are also removed, and some minor interferences (*e.g.*, CrO_4^{--} , which oxidizes Fe^{++} to Fe^{+++}) are also eliminated. MnO_4^- ions also interfere with the test, but a permanganate-nitrite

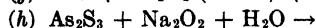
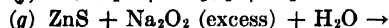
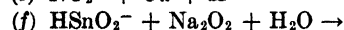
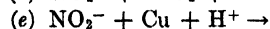
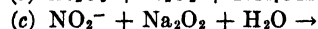
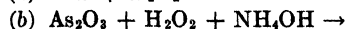
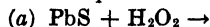
combination is too unstable, even in alkaline medium, to "stand up" for more than a few minutes.

Exercises

1. What reaction would be expected if an excess of NaNO_2 were added to an Al^{+++} solution and the mixture warmed?
2. What are the products when a mixture of $\text{C}_2\text{H}_3\text{O}_2^-$ and NO_2^- is heated with acidified KMnO_4 solution?
3. Name a reagent that will separate OH^- and CO_3^{--} ions.
4. What are the products when an excess of Al^{+++} solution is added to a solution containing NaOH and Na_2CO_3 ?
5. What would you expect if a solution of BiCl_3 were treated with an excess of $\text{NaC}_2\text{H}_3\text{O}_2$ and boiled?
6. The acetate of what trivalent cation is stable against hydrolysis?
7. Why is $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ a buffer for both acids and bases?
8. Write the expression for the equilibrium existing in an aqueous solution of NO_2 .
9. Explain the difference in color of the gases evolved when dilute NaNO_2 is acidified with (a) dilute $\text{HC}_2\text{H}_3\text{O}_2$ and (b) concentrated H_2SO_4 .
10. Name five sodium salts whose solutions give tests for the OH^- ion.
11. Why should metallic copper dissolve more rapidly in M HNO_2 than in M HNO_3 ?
12. What complex nitrite is used as a precipitant for K^+ ? What ions does the reagent contain?
13. Complete the following equation: $\text{NO}_2^- + \text{Fe}^{++} + \text{H}^+ \rightarrow$
14. Suppose an unknown were made up of KNO_2 and KMnO_4 in the molar ratio 5:2 and dissolved in excess of dilute H_2SO_4 . What ions would be present?
15. In general, the salts of which two cation groups give basic solutions?
16. Name two ethyl esters whose odors might be mistaken for ethyl acetate.
17. Explain (a) the color obtained upon acidifying a cold dilute solution of a nitrite and (b) the evolution of a colorless gas upon rise of temperature.
18. The anion tests (except with basic indicators) on a Ca^{++} compound are negative. How would you proceed to determine the identity of the compound?
19. The carbonates of what cations give a red color with phenolphthalein solution?
20. What is the phenolphthalein reaction of a mixture of ZnO (excess) and Na_2CO_3 ? Explain your answer.
21. Calculate the percentage composition of "25-volume" hydrogen peroxide.
22. Calculate the volume (standard conditions) of oxygen evolved by 1 l. of 3 per cent H_2O_2 when it is treated with an excess of (a) $\text{MnO}_4^- + \text{H}^+$, (b) platinum black.
23. How would you go about proving that $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ is a "true peroxide"?

24. How would you determine whether HBO_3 were a "true" or "false" perboric acid?

25. Complete the following equations:



26. Write (a) two equations in which NO_2^- functions as a reducing agent, (b) two equations in which HNO_2 functions as an oxidizing agent.

27. The formula of precipitated magnesium carbonate is usually written " MgCO_3 ." This is incorrect; for, upon heating, water is given off. Quantitative analysis shows the following composition: 45.15 per cent MgO and 36.13 per cent CO_2 . Calculate the true formula.

Ans.: $\text{Mg}(\text{OH})_2 \cdot 3\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$.

28. Basic lead sulfate analyzes 78.71 per cent Pb and 18.25 per cent SO_4 . Calculate its formula.

29. Identify the following anions of Group II:

(a) An anion that gives a fragrant odor with $\text{C}_2\text{H}_5\text{OH}$ + concentrated H_2SO_4 but no red color with FeCl_3 .

(b) An anion that gives a brown precipitate with AgNO_3 , darkening upon boiling.

(c) An anion that gives a colorless, odorless gas with urea in the presence of dilute H_2SO_4 .

30. Complete and balance the following equation: $\text{MnO}_2 + \text{NO}_2^- + \text{H}^+ \rightarrow \text{Mn}^{++}$, etc. How many cubic centimeters of M NaNO_2 would be needed to dissolve 0.087 g. of MnO_2 ?

31. What is the composition of the solution obtained by adding 5 cc. of M NaNO_2 to a mixture of 10 cc. of 0.3 M KI and 2 cc. of 6 M $\text{HC}_2\text{H}_3\text{O}_2$?

32. How would the presence of excess NO_2^- affect the test for S^{--} ? Explain by means of equations. How would you proceed to test for S^{--} ?

33. Calculate the percentage ionization of 0.5 M $\text{HC}_2\text{H}_3\text{O}_2$ if the ionization constant is 1.8×10^{-5} ?

CHAPTER XXII

ANION GROUP III

This group consists of the anions whose Ag^+ and Ba^{++} salts are insoluble in water but soluble in dilute HNO_3 . It is divided into two subgroups IIIa and IIIb on the basis of whether the Ag^+ salts are white or colored.

IIIa (Ag^+ salts white)	IIIb (Ag^+ salts colored)
Carbonate, CO_3^{--}	Phosphate, PO_4^{---}
Oxalate, $\text{C}_2\text{O}_4^{--}$	Arsenate, AsO_4^{---}
Tartrate, $\text{C}_4\text{H}_4\text{O}_6^{--}$	Arsenite, AsO_3^{---}
Sulfite, SO_3^{--}	Chromate, CrO_4^{--}
Thiosulfate, $\text{S}_2\text{O}_3^{--}$	Dichromate, $\text{Cr}_2\text{O}_7^{--}$
Borate, BO_3^{---}	

CARBON

Carbon is sometimes met in the course of a qualitative analysis, and a few statements concerning its detection are in order.

Carbon occurs in iron alloys as the carbide, Fe_3C (cementite), and cast iron contains carbon in the form of graphite. Various other substances contain carbon—*e.g.*, black gunpowder, printing ink, lubricants, automobile tires, polishes for stoves and shoes, and even candy.

Amorphous Carbon.—Free carbon is usually found in the so-called *amorphous* form, as charcoal, lampblack, etc. X-ray examination has shown that these forms are not truly amorphous but consist of graphite dispersed in tarry materials that act as a binder.

Carbon in its amorphous form is detected by (1) its appearance, (2) its absorptive powers (animal charcoal, for example), and (3) the formation of CO_2 upon combustion. One method of testing for free carbon is to drop a minute amount of the material into a little fused KClO_3 or KNO_3 in a test tube or crucible. A harmless explosion follows.

Graphite.—Graphite consists of gray, hexagonal plates, which rub off easily; hence it has a greasy feeling and makes a mark upon paper. It occurs native in many parts of the world but is now

manufactured on a large scale by heating coke to a high temperature in an electric furnace. It is used as a lubricant, a pigment in pencils and paints, as a constituent of crucibles and furnace linings, and as an electrode material for arc lights and electric cells.

Graphite does not react with dilute acids or alkalies, but with concentrated HNO_3 it slowly forms a yellow-to-green substance called *graphitic acid*. Stronger oxidizing agents, such as $\text{H}_2\text{Cr}_2\text{O}_7$, HClO_3 , etc., oxidize graphite to CO_2 . At high temperatures, it burns to CO_2 .

It is usually detected by its physical properties and by the formation of CO_2 when it is strongly heated in a current of oxygen.

Diamonds.—The crystalline variety of carbon occurs in a clear form, used as a gem, and in a black form, used as an abrasive. When heated to a high temperature in oxygen, diamonds burn to CO_2 . Diamonds can hardly be tested by chemical means, for that would involve their destruction. The following physical tests may be employed: (1) *Hardness*. The diamond is the hardest known substance. However, the scratching of glass is not a sufficient test, for several other substances will do that. (2) *Density*. The diamond has a density of 3.51, and this property has been used in its detection. (3) *Index of refraction*. The diamond owes its brilliance to its high index of refraction. Jewelers have instruments by which the index of refraction of a gem may be measured. (4) *Fluorescence*. In the presence of radioactive substances, diamonds show a brilliant luminescence. (5) *Crystal structure*. Diamonds may be definitely identified by the "patterns" given upon X-ray examination. In spite of the foregoing tests, the usual procedure is an optical examination by an expert. He cannot exactly describe it, but a diamond "looks different" from other substances.

CARBON MONOXIDE

Carbon monoxide, CO , is a colorless, odorless gas, liquefying at -190° . It is very poisonous, as small a concentration as 0.1 per cent being fatal. The gas forms with the hemoglobin of the blood a stable compound called *carboxyhemoglobin*, with the result that the elimination of the poison from the human system is slow.

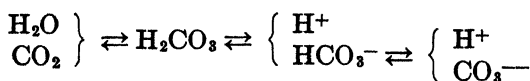
The gas is prepared by (1) the incomplete combustion of coal and other carbonaceous material, (2) passing CO_2 over red-hot carbon, (3) passing steam over red-hot coke, and (4) heating formates, oxalates, or ferrocyanides with concentrated H_2SO_4 . It is the toxic component in the exhaust gases of gasoline engines.

Though carbon monoxide is an active reducing agent at high temperatures, it is decidedly inert at ordinary temperatures, so that its detection is difficult. For low concentrations, the oxidation to CO_2 is not sensitive. The following are the more important tests: (1) CO reduces palladium chloride, PdCl_2 , to metallic palladium, which may be further tested by the formation of "molybdenum blue" with MoO_4^- . (2) Iodic acid, HIO_3 , and iodine pentoxide, I_2O_5 , are reduced to free iodine, which may be detected by the color of their solutions. (3) With blood it forms red carboxyhemoglobin, which gives a characteristic absorption spectrum. The latter is a physiological test, but it is highly sensitive and specific.

CARBONATE

The Ions.—There are two carbonate ions: the normal carbonate, CO_3^- , and the hydrogen carbonate, HCO_3^- . The latter is frequently called *bicarbonate*. As will shortly be seen, these ions are in ready equilibrium with each other, so that each gives the reactions of both.

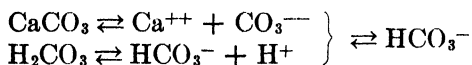
The Acid.—Carbonic acid, H_2CO_3 , exists only in solution. Upon concentrating or warming, it dissociates into water and carbon dioxide. Solutions of H_2CO_3 are prepared by saturating water with CO_2 , a solution that is approximately 0.03 molar being thus obtained. The acid ionizes in steps, forming HCO_3^- and CO_3^- ions. All of these equilibria may be collected as follows:



The constant for the primary ionization is 3×10^{-7} , and for the secondary ionization is 6×10^{-11} . From the first constant, it appears that H_2CO_3 , at its best, is a very weak acid. The secondary ionization is so slight that it is negligible in most cases.

Upon heating, the above equilibria are displaced to the left, owing to the volatility of the CO_2 . As a result, carbonates may be completely removed from a solution by acidifying and boiling.

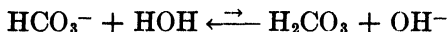
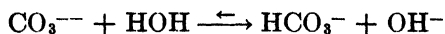
Solubilities.—The normal carbonates soluble in water are Na_2CO_3 , K_2CO_3 , and $(\text{NH}_4)_2\text{CO}_3$; other normal carbonates are insoluble. Several carbonates insoluble in water are soluble in excess H_2CO_3 , forming hydrogen carbonates; *e.g.*, $\text{Ca}(\text{HCO}_3)_2$, $\text{Sr}(\text{HCO}_3)_2$, $\text{Ba}(\text{HCO}_3)_2$, $\text{Fe}(\text{HCO}_3)_2$, etc. The reaction seems to be mainly due to a displacement in the dissociation of CaCO_3 by the withdrawal of the CO_3^{--} ion; *e.g.*,



A low ionization of $\text{Ca}(\text{HCO}_3)_2$ may be involved to some extent. All hydrogen carbonates appear to be soluble.

Normal carbonates generally dissolve readily in acids with the evolution of CO_2 . Exceptions are the mineral carbonates, such as MgCO_3 (magnesite) and $\text{MgCO}_3 \cdot \text{CaCO}_3$ (dolomite), which dissolve slowly.

Hydrolysis of Carbonates.—Owing to low ionization of molecular H_2CO_3 and the hydrogen carbonate ion HCO_3^- , there is a tendency for the carbonate ion to withdraw H^+ ions from the solvent water, leaving an excess of OH^- ions in the solution. Accordingly, their solutions are basic.



The magnitude and direction of the arrows indicate that solutions of normal carbonates are more alkaline than solutions of hydrogen carbonates.

In molar solution of Na_2CO_3 and K_2CO_3 , the concentration of the OH^- ion is 0.012; *i.e.*, they are 1.2 per cent hydrolyzed. The OH^- concentration in *M* NaHCO_3 and *M* KHCO_3 is about 1.8×10^{-4} —a hydrolysis of 0.018 per cent. Hydrogen carbonates like $\text{Pb}(\text{HCO}_3)_2$ are not sensibly basic, because the cations tend to combine with any free OH^- ions, forming weak bases, such as $\text{Pb}(\text{OH})_2$.

Reactions.—As explained on page 287, carbonates cannot be precipitated from neutral solutions by means of H_2CO_3 (*i.e.*, by saturating with CO_2). This is due, not only to (1) the very low concentration of CO_3^{--} ions in H_2CO_3 solution, but further to (2) the fact that the increasing H^+ ion concentration tends to reverse the reaction; *e.g.*, $\text{Ca}^{++} + \text{H}_2\text{CO}_3 \rightleftharpoons \text{CaCO}_3 + 2\text{H}^+$. In precipitation from slightly basic solutions, the action is apt to be incomplete. The increase in acidity tends to convert CO_3^{--} ions into HCO_3^- , and hydrogen carbonates are generally soluble.

Detection.—The CO_3^{--} ion does not form a distinctive precipitate with any cation. That is, carbonate precipitates do not differ in appearance, solubility, etc., from the corresponding oxalates, phosphates, etc. The best that can be done is to break the CO_3^{--} ion down into gaseous CO_2 , which does show a distinctive behavior. This gas may be detected by passing it into $\text{Ca}(\text{OH})_2$ solution, with which it forms a white precipitate of CaCO_3 . $\text{Ba}(\text{OH})_2$ solution is sometimes used instead of the $\text{Ca}(\text{OH})_2$.

A simple apparatus for this test is shown in Fig. 30. The substance to be tested is placed in the 50-cc. flask A, and dilute H_2SO_4 is introduced through the thistle tube B. The gas evolved is passed through the $\text{Ca}(\text{OH})_2$ solution in the test tube C. The CaCO_3 appears as a milky precipitate.

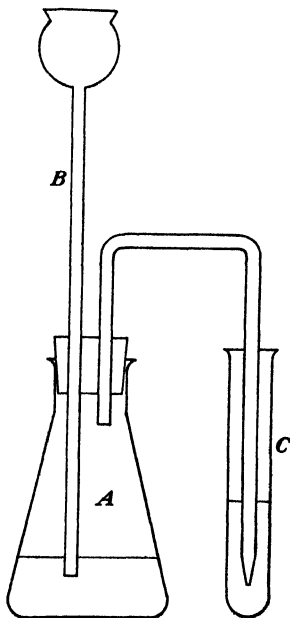


FIG. 30.—Evolution of CO_2 apparatus.

Another procedure is to acidify the material in an open vessel—preferably a test tube—and test the gas evolved with a stirring rod that has been dipped in $\text{Ca}(\text{OH})_2$ or $\text{Ba}(\text{OH})_2$. The first procedure has the advantage of giving greater sensitiveness; more of the gas evolved is brought into contact with the reagent. This same setup is also used in testing for $\text{C}_2\text{O}_4^{--}$, SO_3^{--} , and $\text{S}_2\text{O}_3^{--}$. It should be compact, so that the gas will not be lost in a large

flask or long delivery tube but will be brought into contact with the reagent.

Interferences.—Certain interferences must be considered in the test for CO_3^{--} .

1. The acid used to liberate the CO_2 must not be volatile, because it would tend to distill over and neutralize the $\text{Ca}(\text{OH})_2$ or redissolve any CaCO_3 already formed. For this reason, H_2SO_4 is generally used.

2. The flask should not be overheated. It is possible to boil the solution hard enough to carry over enough H_2SO_4 in the spray to form a precipitate of CaSO_4 in the $\text{Ca}(\text{OH})_2$ solution.

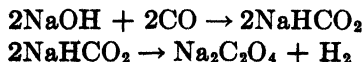
3. Sulfitcs sometimes interfere by forming a precipitate of CaSO_3 in the $\text{Ca}(\text{OH})_2$ solution. This can be prevented by adding an oxidizing agent (*e.g.*, KMnO_4) to the material in the flask before introducing the acid. SO_3^{--} ions are thereby oxidized to the nonvolatile H_2SO_4 .

4. If large amounts of CO_2 are produced, the CaCO_3 precipitate may redissolve, forming soluble $\text{Ca}(\text{HCO}_3)_2$.

5. Certain mineral carbonates (*e.g.*, dolomite, $\text{CaCO}_3 \cdot \text{MgCO}_3$) dissolve very slowly in dilute acids, so that CO_2 is liberated in small quantity. In such cases, it is desirable to make the test on some of the material that has been pulverized in a mortar.

OXALATE

Oxalates received their name from their occurrence in the sorrel (*oxalis*) family of plants. They very seldom occur in minerals (*i.e.*, ores), since they would be destroyed by the high temperatures that have prevailed in the earth's crust. Oxalates are mildly poisonous but not toxic enough to prevent certain plants in which they occur (*e.g.*, rhubarb) from being edible. Oxalates are extensively used in the dyeing and leather industries, for which they are manufactured as the sodium salt (1) by heating sawdust with NaOH at 200 to 220° , and (2) by heating sodium formate to 200° . In the latter process, the sodium formate is formed by heating NaOH with CO under a pressure of 6 to 10 atm. The steps in the process may be represented thus:



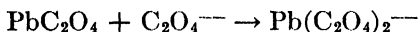
The Acid.—Oxalic acid is a white crystalline solid—usually the dihydrate, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. It is soluble in water, forming a moderately strong acid. Its ionization constants are as follows: $K_1 = 3.8 \times 10^{-2}$, and $K_2 = 4.9 \times 10^{-5}$. Consequently the H^+ and $\text{C}_2\text{O}_4^{--}$ concentrations in M $\text{H}_2\text{C}_2\text{O}_4$ are 0.177 and 0.000049 respectively.

Anhydrous $\text{H}_2\text{C}_2\text{O}_4$ sublimes at high temperatures with slight decomposition. Upon heating with concentrated H_2SO_4 , it decomposes as follows:



It is unaffected by boiling with dilute acids (*cf.* CO_3^{--}).

Solubilities.—All oxalates are insoluble in water except $\text{Na}_2\text{C}_2\text{O}_4$, $\text{K}_2\text{C}_2\text{O}_4$, $(\text{NH}_4)_2\text{C}_2\text{O}_4$, and $\text{Fe}_2(\text{C}_2\text{O}_4)_3$. Many of the oxalates insoluble in water are soluble in excess $\text{C}_2\text{O}_4^{--}$ ions, owing to the formation of complex anions; *e.g.*,

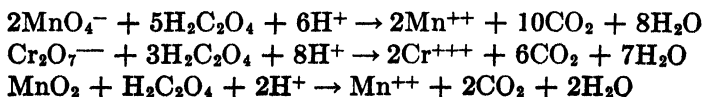


CaC_2O_4 , SrC_2O_4 , and BaC_2O_4 are the most important exceptions to this behavior.

Alkaline Earth Oxalates.—The most important of the insoluble oxalates is CaC_2O_4 , white, insoluble in $\text{HC}_2\text{H}_3\text{O}_2$, but soluble in HCl or HNO_3 . The Ba^{++} and Sr^{++} salts resemble CaC_2O_4 but are slightly more soluble in water. As a result, they are not completely precipitated in $\text{HC}_2\text{H}_3\text{O}_2$ solution.

Silver Oxalate.— $\text{Ag}_2\text{C}_2\text{O}_4$ is a white, curdy salt, readily soluble in NH_4OH and in dilute HNO_3 .

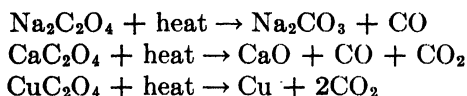
Reducing Action.—Oxalic acid is a weak reducing agent: $\text{H}_2\text{C}_2\text{O}_4 + [\text{O}] \rightarrow \text{H}_2\text{O} + 2\text{CO}_2$. It is too weak to react with weak oxidizing agents like H_2O_2 and even I_2 . It is only slowly attacked by concentrated HNO_3 , unless there is present some substance (*e.g.*, Mn^{++}) that acts as a catalyst. It reacts rapidly with strong oxidizing agents, such as HMnO_4 , $\text{H}_2\text{Cr}_2\text{O}_7$, and MnO_2 in the presence of an acid, particularly in the presence of the catalyst Mn^{++} .



The catalytic action of the Mn^{++} ion is not definitely understood. The Hg^{++} ion acts in a similar way.

Oxalates are not oxidized in alkaline medium by even such powerful oxidizing agents as Na_2O_2 . This seems to indicate that the reducing agent is the $\text{H}_2\text{C}_2\text{O}_4$ molecule and not the $\text{C}_2\text{O}_4^{--}$ ion.

Ignition.—Oxalates are decomposed upon ignition, sometimes with slight charring. CO , and sometimes CO_2 , are formed, usually leaving a residue of carbonate or oxide. Metallic residues are left in cases where the oxides are easily reduced; *e.g.*,



Detection.—Like CO_3^{--} and other anions, the $\text{C}_2\text{O}_4^{--}$ ion gives no precipitation reaction that is sufficiently characteristic to be used as a test. The usual procedure is to oxidize it to CO_2 by means of HMnO_4 and to test for that gas by bubbling it through $\text{Ca}(\text{OH})_2$ or $\text{Ba}(\text{OH})_2$ solution. The test is suitably carried out in the setup used in the detection of CO_3^{--} (Fig. 30, page 363).

Interferences.—Carbonates and tartrates also give off CO_2 when treated with acidified KMnO_4 and must previously be separated. The CO_3^{--} may be removed by acidification and warming. The $\text{C}_4\text{H}_4\text{O}_6^{--}$ may be separated from $\text{C}_2\text{O}_4^{--}$ (1) by precipitating the latter as CaC_2O_4 by CaCl_2 in acetic acid solution, or (2) by adding CaCl_2 and an excess of cold NaOH , precipitating CaC_2O_4 . In either case, the CaC_2O_4 is well washed before the HMnO_4 test is applied.

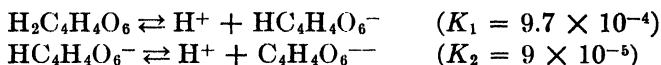
Fluorides interfere by giving off HF , which may form a precipitate of CaF_2 (see page 408). This precipitate differs from CaCO_3 in being insoluble in $\text{HC}_2\text{H}_3\text{O}_2$. This interference may be obviated by adding CaCl_2 to the mixture in the generator.

TARTRATE

Tartrates are obtained from the deposits of crude cream of tartar, $\text{KHC}_4\text{H}_4\text{O}_6$, and calcium tartrate, $\text{CaC}_4\text{H}_4\text{O}_6$, which form in wine barrels. Another name for these deposits is *argols*. Tartrates are mainly used in baking powders, medicines, and mordants for dyes.

The Acid.—Tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, is a white solid, readily soluble in water and in alcohol. It melts at 135° ; at somewhat higher temperatures, it chars, leaving a residue of charcoal and giving off vapors having the odor of "burnt sugar." It is decomposed by concentrated H_2SO_4 , giving off CO_2 , CO , SO_2 , and other gases and leaving a residue of impure carbon. Evidently the action of the H_2SO_4 is both dehydration and oxidation. No equation can be written for the reaction.

Tartaric acid ionizes in steps, thus:

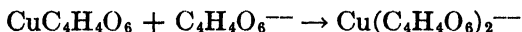


As indicated by these ionization constants, tartaric acid is a fairly strong acid. Molar $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ is ionized slightly more than 3 per cent; and the $\text{HC}_4\text{H}_4\text{O}_6^-$ ion is ionized enough for $\text{KHC}_4\text{H}_4\text{O}_6$ to taste distinctly sour.

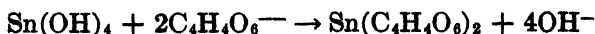
The two tartrate anions form well-defined series of salts. Salts containing the $\text{HC}_4\text{H}_4\text{O}_6^-$ -group are generally known as *bitartrates*, though *hydrogen tartrates* or *acid tartrates* seem preferable names. The salts containing the $\text{C}_4\text{H}_4\text{O}_6^{--}$ -group are called *normal*, or sometimes *neutral tartrates*.

Solubilities.—Of the normal tartrates, $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$, $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$, and $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$ are soluble in water, while the remaining tartrates are insoluble. Of the acid tartrates, $\text{NaHC}_4\text{H}_4\text{O}_6$ is soluble, whereas $\text{KHC}_4\text{H}_4\text{O}_6$ and $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$ are slightly soluble.

Many insoluble tartrates dissolve in excess $\text{C}_4\text{H}_4\text{O}_6^{--}$ ions, presumably forming complex anions; *e.g.*,



The tartrates of Mn^{++} , Co^{++} , Ni^{++} , Fe^{++} , and Pb^{++} behave similarly. In addition, there are a number of cations whose hydroxides dissolve in excess $\text{C}_4\text{H}_4\text{O}_6^{--}$ anions; *e.g.*, $\text{Fe}(\text{OH})_3$ gives with $\text{C}_4\text{H}_4\text{O}_6^{--}$ a tartrate of undetermined composition. $\text{Sn}(\text{OH})_4$, $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{Sb}(\text{OH})_3$, and several other insoluble hydroxides dissolve in a similar fashion. The products of these reactions are sometimes represented as molecules; *e.g.*,



However, the excess of $\text{C}_4\text{H}_4\text{O}_6^-$ required seems to indicate that the product must be an anion of complex composition.

Numerous applications of this solvent action of $\text{C}_4\text{H}_4\text{O}_6^-$ are found in analytical chemistry. Tartrates are added to prevent the separation of antimonyl precipitates in the Tin subgroup. Fehling's solution, used in the determination of sugars, consists of an alkaline cupric tartrate solution. Fe^{+++} ions are separated from Al^{+++} ions by precipitation of Fe_2S_3 by $(\text{NH}_4)_2\text{S}$ in the presence of $\text{C}_4\text{H}_4\text{O}_6^-$.

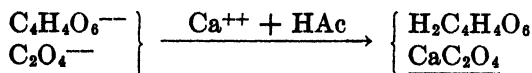
Reactions.—Some of the more important reactions of tartrates are as follows.

Potassium Hydrogen Tartrate.— K^+ ions give no precipitate with $\text{C}_4\text{H}_4\text{O}_6^-$ in neutral or alkaline solution. In the presence of $\text{HC}_2\text{H}_3\text{O}_2$ or other weak acid, a crystalline precipitate of $\text{KHC}_4\text{H}_4\text{O}_6$ forms slowly or after standing, depending on the concentration of the ions involved.



This precipitate is readily soluble in strong acids, for the excess H^+ ions combine with practically all of the $\text{C}_4\text{H}_4\text{O}_6^-$ to form molecular $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$. It also dissolves in OH^- , owing to the removal of the H^+ ions from the left side of the above equation. The precipitation of $\text{KHC}_4\text{H}_4\text{O}_6$ is sometimes used for the separation of $\text{C}_4\text{H}_4\text{O}_6^-$ from other anions, such as $\text{C}_2\text{H}_3\text{O}_2^-$ and C_2O_4^- . The separation is never complete, however, unless care is taken to regulate the acidity properly and to allow the mixture to stand for some time before filtering.

Calcium Tartrate.—Excess of Ca^{++} ions precipitates $\text{C}_4\text{H}_4\text{O}_6^-$ in neutral solution, forming white $\text{CaC}_4\text{H}_4\text{O}_6$. As in many other cases (see preceding paragraphs), the precipitate is soluble in excess $\text{C}_4\text{H}_4\text{O}_6^-$. It is also soluble in acids, owing to the formation of un-ionized $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$. Even $\text{HC}_2\text{H}_3\text{O}_2$ will dissolve it. This reaction may be used to separate $\text{C}_4\text{H}_4\text{O}_6^-$ from C_2O_4^- .



A very unusual type of reaction is the solubility of $\text{CaC}_4\text{H}_4\text{O}_6$ in cold NaOH , from which CO_3^- ions have been removed by a

few drops of $\text{Ca}(\text{OH})_2$ or $\text{Ba}(\text{OH})_2$. Upon heating, the $\text{CaC}_4\text{H}_4\text{O}_6$ is reprecipitated.

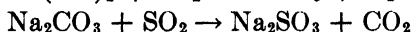
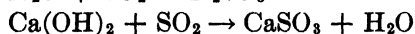
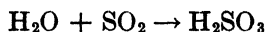
Oxidation by Permanganate.— $\text{C}_4\text{H}_4\text{O}_6^{--}$ is oxidized by acidified KMnO_4 , liberating a mixture of CO_2 and CO . The reaction is not a smooth one, and no equation can be written. This reaction interferes with the detection of $\text{C}_2\text{O}_4^{--}$ by means of KMnO_4 .

Reduction of Ammoniacal Silver Solution.—As just suggested, $\text{C}_4\text{H}_4\text{O}_6^{--}$ is a reducing agent, more active in alkaline than in acid solution. It has no effect on Ag^+ in acid solution; but, in the presence of NH_4OH , metallic silver is precipitated. Under proper conditions, the silver comes out as a bright mirror.

Detection.—There is no one reaction that is an absolute test for $\text{C}_4\text{H}_4\text{O}_6^{--}$. The analyst must depend upon a series of tests, as follows: (1) charring when heated on porcelain or platinum; (2) a white crystalline precipitate with K^+ in the presence of $\text{HC}_2\text{H}_3\text{O}_2$; (3) a precipitate with Ca^{++} , soluble in cold NaOH (free from Na_2CO_3), reprecipitated upon boiling; (4) mirror formation with $\text{Ag}(\text{NH}_3)_2^+$. There is no other anion that gives all these reactions. Consequently the combined effect is highly conclusive.

SULFITE

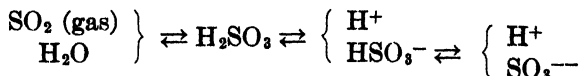
Sulfites are formed by the action of SO_2 on oxides, hydroxides, carbonates, etc.; *e.g.*,



On account of their ready oxidizability, they never occur in nature—in minerals, for example.

The Acid.—A solution of sulfurous acid, H_2SO_3 , is formed by saturating water with SO_2 . The solution is unstable and dissociates upon concentrating or heating.

Sulfurous acid ionizes in steps, forming hydrogen sulfite (bisulfite) ions HSO_3^- , and sulfite ions SO_3^{--} . The ionization constants are as follows: $K_1 = 1.7 \times 10^{-2}$, and $K_2 = 5 \times 10^{-6}$. The total equilibrium may be expressed thus:

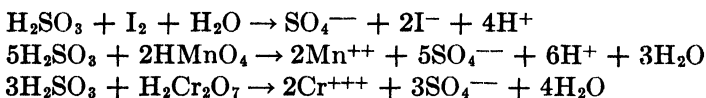


Equilibrium may be displaced by heating to expel the volatile

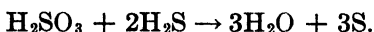
SO₂, though prolonged boiling is necessary for its complete removal. It should be noticed that H₂SO₃ is a fairly strong acid; doubtless the high degree of ionization is responsible for the difficulty in boiling out the SO₂.

Solubilities.—The normal sulfites, Na₂SO₃, K₂SO₃, and (NH₄)₂SO₃, are soluble in water. The other normal sulfites are insoluble, or nearly so. The most insoluble sulfite seems to be SrSO₃, which has a solubility of about 0.002 mole per liter. The sulfites of Ca⁺⁺, Sr⁺⁺, Ba⁺⁺, and Mg⁺⁺ are soluble in excess of SO₂ solution, owing to the formation of the soluble hydrogen sulfites, but are reprecipitated upon boiling (*cf.* Ca(HCO₃)₂, page 362). The hydrogen sulfites of Na⁺, K⁺, and NH₄⁺ are also soluble, and may be obtained in the solid form by evaporation of the solvent.

Oxidation.—Sulfites, especially in acid solution, are active reducing agents, reacting with oxidizing agents to form sulfate ions, SO₄[—]; *e.g.*,



On the other hand, they act as oxidizing agents with certain powerful reducing agents; *e.g.*,



Detection.—The SO₃[—] ion is detected by the formation of SO₂ when the material is acidified and warmed. This gas may be detected by (1) its odor or (2) its formation of SO₄[—] upon oxidation. The odor test should be made carefully, for even small concentrations of the gas are very unpleasant. The oxidation-to-SO₄[—] test is best made with the generator outfit described under carbonate (page 363). The SO₂ is distilled into a very dilute solution of KMnO₄ containing dilute HNO₃ and Ba(NO₃)₂. The purple MnO₄[—] is reduced to colorless Mn⁺⁺, and the SO₄[—] formed reacts with Ba⁺⁺ to form a white precipitate of BaSO₄.

Interferences.—S[—] and S₂O₃[—] ions interfere with this test. Upon acidification, S[—] becomes H₂S, which decolorizes HMnO₄ with the formation of SO₄[—]; and S₂O₃[—] gives SO₂. These interfering ions may be removed as follows: The solution is shaken

with a suspension of CdCO_3 , precipitating the S^- as yellow CdS . The filtrate is then treated with $\text{Sr}(\text{NO}_3)_2$ solution and allowed to stand several hours. This precipitates the SO_3^- as SrSO_3 , leaving the S_2O_3^- still in solution. The S_2O_3^- may then be detected by the formation-of- SO_2 test described on the preceding page.

THIOSULFATE

Thiosulfates were formerly called *hyposulfites*, owing to a misapprehension as to their constitution. For example, sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, was known as *hyposulfite of soda*. More recently, true hyposulfites have been prepared (e.g., sodium hyposulfite, Na_2SO_2), and the S_2O_3^- -group is now generally known as thiosulfate.

Thiosulfates are usually prepared by boiling sulfur with a solution of a sulfite: $\text{S} + \text{SO}_3^- \rightarrow \text{S}_2\text{O}_3^-$.

Thiosulfates are used industrially to neutralize the excess chlorine in bleaching cotton cloth and as a solvent for the unchanged silver halide in photography.

The Acid.—Thiosulfuric acid, $\text{H}_2\text{S}_2\text{O}_3$, is unstable, and the pure acid has never been prepared. Even in dilute solution, it decomposes rapidly, thus: $\text{H}_2\text{S}_2\text{O}_3 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + \text{S}$.

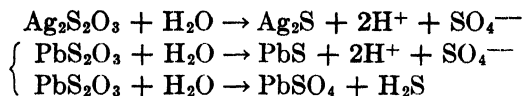
Solubilities.—Most of the thiosulfates are soluble in water. $\text{Ag}_2\text{S}_2\text{O}_3$, PbS_2O_3 , HgS_2O_3 , and BaS_2O_3 have the lowest solubilities. As noted in the following paragraphs, $\text{Ag}_2\text{S}_2\text{O}_3$ and PbS_2O_3 are soluble in excess of S_2O_3^- ions.

Reactions.—Certain of the reactions of S_2O_3^- are so unusual as to require special attention.

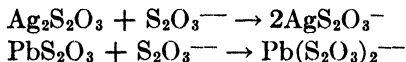
1. *With Acids.*—Acids decompose thiosulfates, liberating SO_2 and precipitating sulfur.

2. *With Ba^{++} .*— S_2O_3^- ions react with Ba^{++} to form white crystalline BaS_2O_3 , difficultly soluble in cold, but fairly soluble in warm water. Cooling and standing therefore favor the separation of this precipitate. Shaking, or rubbing the inside wall of the test tube, also helps.

3. *With Ag^+ and Pb^{++} .*—These cations unite with S_2O_3^- in the cold, forming white $\text{Ag}_2\text{S}_2\text{O}_3$ and white PbS_2O_3 . Upon standing, and more rapidly upon warming, these salts react with water, forming sulfides (or sulfates).

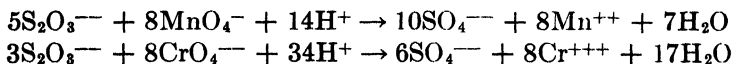


With excess of $\text{S}_2\text{O}_3^{--}$ ions, $\text{Ag}_2\text{S}_2\text{O}_3$ and PbS_2O_3 redissolve, presumably forming complex anions; *e.g.*,

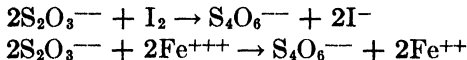


4. *With Oxidizing Agents.*—Thiosulfates are mild reducing agents, the oxidation product being determined by the strength of the oxidizing agent.

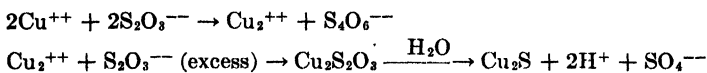
Strong oxidizing agents oxidize the $\text{S}_2\text{O}_3^{--}$ ion to sulfate, SO_4^{--} ; *e.g.*,



Weak oxidizing agents oxidize $\text{S}_2\text{O}_3^{--}$ to the tetrathionate ion, $\text{S}_4\text{O}_6^{--}$; *e.g.*,

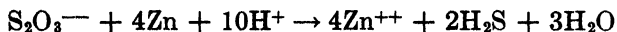


Cupric solutions are first reduced to the colorless cuprous form, which decomposes rapidly upon heating, precipitating a sulfide.



Note that the precipitate is Cu_2S and not CuS .

5. *With Reducing Agents.*—If $\text{S}_2\text{O}_3^{--}$ ions are treated with very strong reducing agents, such as zinc in acid solution, the $\text{S}_2\text{O}_3^{--}$ is reduced to H_2S .



This reaction should be kept in mind in making the test for insoluble sulfides (see page 338).

Detection.—The following reactions are used in the detection of the $\text{S}_2\text{O}_3^{--}$ ion: (1) The separation of a precipitate of white sulfur and the evolution of SO_2 upon acidification. The SO_2 may be detected as in the case of SO_3^{--} . (2) A failure to form a

precipitate with Sr^{++} (distinction from SO_3^{--}). (3) The formation of black Ag_2S upon addition of AgNO_3 and warming. (4) The reduction of HMnO_4 with or without the separation of sulfur.

BORATE

There are several borate ions: orthoborate, BO_3^{--} ; metaborate, BO_2^- ; and pyroborate (tetraborate), $\text{B}_4\text{O}_7^{--}$. These seem to be in ready equilibrium with one another, for they give identical reactions.

The Acid.—Boric acid, H_3BO_3 (the "boracic acid" of medicine), is a white crystalline solid. It is only moderately soluble in water—about 55 g., or 0.9 mole per liter at room temperature. Upon ignition, it loses water and leaves B_2O_3 as a glassy residue. The fused oxide has the property of dissolving most metallic oxides but none of the nonmetallic oxides. H_3BO_3 is somewhat volatile and may be expelled from solution by prolonged boiling. It is said to be volatile in steam, which serves to repress its dissociation into the less volatile oxide: $2\text{H}_3\text{BO}_3 \rightleftharpoons 3\text{H}_2\text{O} (\text{steam}) + \text{B}_2\text{O}_3$.

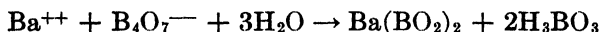
Boric acid is a very weak acid—so weak that a saturated solution may be used as an eyewash. The constant for its primary ionization is only 2.3×10^{-9} ; the amounts of secondary and tertiary ionization are so small as to be negligible.

Solubilities.—The borates soluble in water are those of the alkali ions Na^+ , K^+ , and NH_4^+ . The others are difficultly soluble in water but dissolve readily in dilute acids, owing to the low ionization of H_3BO_3 . Owing to its low solubility, a precipitate of H_3BO_3 is apt to separate from these solutions, particularly upon cooling.

Borax.—The most important borate is sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, commonly known as *borax*. Upon heating, it loses its water of hydration and leaves anhydrous $\text{Na}_2\text{B}_4\text{O}_7$ as a glassy melt, which is a good solvent for metallic oxides (*cf.* borax beads, page 419). Borax is extensively used in medicine and metallurgy; in the ceramic, tanning, and textile industries; and as a food preservative.

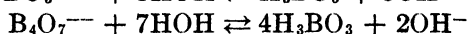
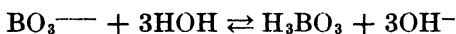
Reactions.—The following analytical reactions should be noted.

1. *Precipitation of Borates.*—All cations, except those of Group V, precipitate the borate from neutral solutions as metaborates; *e.g.*,



$\text{Ba}(\text{BO}_2)_2$ is a white precipitate, easily soluble in acids and NH_4^+ salt solutions.

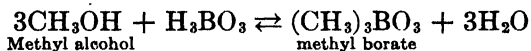
In cold moderately concentrated solution, Ag^+ ions precipitate white AgBO_2 . In dilute solution, the same reactants give brownish Ag_2O . This is due to the hydrolysis of the borate ions.



These equilibria are displaced rightward by the removal of Ag^+ ions by the OH^- : $2\text{Ag}^+ + 2\text{OH}^- \rightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O}$. AgBO_2 is easily soluble in dilute acids, NH_4OH , $\text{S}_2\text{O}_3^{--}$, etc.

2. *Flame Coloration.*—Volatile boron compounds [*e.g.*, H_3BO_3 (not B_2O_3), and certain salts and esters] impart to the colorless Bunsen flame a green color.

3. *Ester Formation.*—Boric acid combines reversibly with alcohols to give "salts" called *esters*; *e.g.*,



The presence of a strong dehydrating agent like H_2SO_4 displaces the equilibrium to the right. These esters are rather volatile. Borates may be completely removed from a solution by adding methyl alcohol and concentrated H_2SO_4 and distilling. These esters are inflammable, burning with the green color characteristic of volatile boron compounds.

4. *Turmeric Reaction.*—Free H_3BO_3 colors turmeric (the extract of an East Indian member of the ginger family) a reddish brown. Upon adding NaOH , the color changes to an olive green.

Detection.—The following reactions are used for the detection of BO_3^{--} : (1) The material is heated with a mixture of ethyl alcohol and concentrated H_2SO_4 , forming ethyl borate, $(\text{C}_2\text{H}_5)_3\text{BO}_3$, which burns with a green flame. Cupric salts interfere by giving a green flame and must be removed by a previous treatment with Na_2CO_3 . (2) A piece of turmeric paper is dipped in an HCl solution of the material and dried on a watch

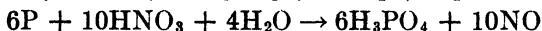
glass over a beaker of boiling water. A red-brown color, turning to a dark green when touched with NaOH, indicates the presence of BO_3 —. Free H_2SO_4 chars turmeric paper; it must therefore be previously removed (*e.g.*, by BaCl_2) before this test is made.

PHOSPHORUS

The element phosphorus seems to exist in several allotropic forms. Of these, the forms known as *white phosphorus* and *red phosphorus* are most common.

White phosphorus is a waxlike solid, slightly soluble in water, but readily soluble in CS_2 and to a less extent in benzene, olive oil, turpentine, etc. When exposed to moist air, it is slowly oxidized and emits a phosphorescent glow. Warmed to 50 to 60°, it takes fire spontaneously, forming white fumes of P_2O_5 . Wet oxidizing agents oxidize it to phosphoric acid, H_3PO_4 . The white form of the element is very poisonous, 0.1 g. being a fatal dose. It was formerly used in the manufacture of matches but has now been replaced by the nonpoisonous sulfide, P_4S_3 . One form of rat poison consists of a small amount of white phosphorus mixed with flour, grease, etc.

Red phosphorus is formed by heating white phosphorus for some time at 250° in an atmosphere of nitrogen. In comparison with white phosphorus, it is very inert. It is insoluble in CS_2 and the other solvents for white phosphorus, it is not poisonous and it does not take fire below about 250°. It is dissolved by HNO_3 , forming phosphoric acid and liberating oxides of nitrogen.



Detection.—In the absence of PO_4 —, uncombined phosphorus may be detected by converting it into H_3PO_4 through boiling with HNO_3 and then testing for the PO_4 — ion with $(\text{NH}_4)_2\text{MoO}_4$ in the usual way. If phosphates are present, they should be extracted by HCl before the HNO_3 treatment is applied.

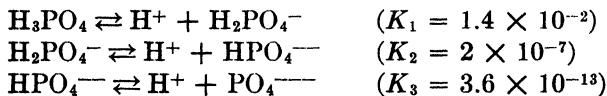
White phosphorus may be detected thus: (1) It may be extracted with CS_2 and the solution allowed to evaporate on filter paper. The finely divided phosphorus will take fire spontaneously. (2) In moist air, the material will show a phosphorescence, visible in a dark room. (3) Its vapors will darken paper

moistened by AgNO_3 solution, owing to the reduction of AgNO_3 to metallic silver: $5\text{Ag}^+ + \text{P} + 4\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + 5\text{H}^+ + 5\text{Ag}$.

PHOSPHATE

There are three phosphate ions: orthophosphate, PO_4^{---} ; metaphosphate, PO_3^- ; pyrophosphate, $\text{P}_2\text{O}_7^{---}$. The last two change into PO_4^{---} upon boiling, so that PO_4^{---} alone needs to be considered.

The Acid.—Orthophosphoric acid, H_3PO_4 , is a tribasic acid, ionizing stepwise as follows:



From these constants it may be calculated that the H^+ concentration in M H_3PO_4 is as follows: 0.1 molar from the primary ionization, 0.0002 molar from the secondary ionization, and 0.00000008 molar from the tertiary ionization; the total is little more than that formed by the primary ionization.

It should be noticed that the dissociation $\text{HPO}_4^{--} \rightleftharpoons \text{H}^+ + \text{PO}_4^{---}$ is very slight—almost as low as the ionization of water. Rather naturally the student would expect it to react faintly acid. On the contrary, it reacts slightly alkaline. The explanation of this surprising fact is that the HPO_4^{--} reacts with water to an appreciable extent, thus: $\text{HPO}_4^{--} + \text{HOH} \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{OH}^-$. The amount of OH^- formed in this way exceeds the H^+ formed in the tertiary ionization.

Phosphoric acid has a high boiling point, and, like H_2SO_4 , is sometimes used to expel low-boiling acids.

Solubilities.—The only phosphates soluble in water are those of the alkali ions Na^+ , K^+ , and NH_4^+ , *e.g.*, Na_3PO_4 , Na_2HPO_4 , NaH_2PO_4 , etc. The normal phosphates of the other cations are insoluble in water but soluble in acids. The easy solubility of normal phosphates is due to the formation of the ions HPO_4^{--} and H_2PO_4^- , whose salts are more soluble than those of PO_4^{---} .

Reactions.—The following reactions are of analytical importance.

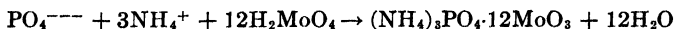
Silver Phosphate.— PO_4^{---} forms with Ag^+ ions yellow Ag_3PO_4 , readily soluble in HNO_3 and NH_4OH . The color of the precipitate is valuable in the identification of the PO_4^{---} ion.

Barium Phosphate.—In neutral solutions, Ba^{++} precipitates white amorphous BaHPO_4 ; in the presence of NH_4OH or dilute alkalis, white $\text{Ba}_3(\text{PO}_4)_2$ is thrown down. Both dissolve readily in acids, even in $\text{HC}_2\text{H}_3\text{O}_2$.

Magnesium Ammonium Phosphate.—From the analytical point of view, this is the most important compound of the PO_4^{---} ion, just as it is the most important compound of the Mg^{++} ion. Both ions are separated from other substances in the MgNH_4PO_4 form. See pages 302 to 303 for its discussion.

Ferric Phosphate.—See page 258 for a description of the properties of this compound.

Detection.—The most valuable reaction for the detection of PO_4^{---} ions is the one with an HNO_3 solution of $(\text{NH}_4)_2\text{MoO}_4$, forming a yellow precipitate, frequently called *ammonium phosphomolybdate*.



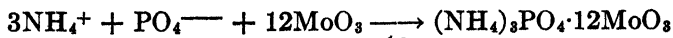
Heat aids in the formation of this precipitate, which is insoluble in HNO_3 but easily soluble in NH_4OH . Arsenate ions AsO_4^{---} form a similar precipitate and must be removed before making the test.

The student should be warned that the molybdic acid reagent is unstable and is apt to decompose, precipitating the H_2MoO_4 as white or yellowish white molybdic anhydride, MoO_3 . The resultant solution may contain no MoO_4^{---} ions and give no test with PO_4^{---} . In case of doubt as to the condition of the reagent, the latter should be checked by making tests on Na_2HPO_4 or other solution known to contain PO_4^{---} .

The mechanism of the above reaction may be understood by assuming that MoO_3 is a chief reactant. As is seen from the interlocking equilibriums



the concentration of MoO_3 increases with the square of the H^+ concentration. The total equation would be written thus:



As indicated, the reaction is slightly reversible. Consequently, complete precipitation calls for excesses of NH_4^+ and MoO_3 , and the latter calls for excesses of MoO_4^{---} and H^+ (from HNO_3).

ARSENATE, ARSENITE

A number of anions containing arsenic are recognized, corresponding to the various arsenates and arsenites known in the solid state. They are listed below according to the valence of the arsenic.

Pentavalent Arsenic	Trivalent Arsenic
Orthoarsenate, AsO_4^{---}	Orthoarsenite, AsO_3^{---}
Dihydrogen arsenate, H_2AsO_4^-	
Monohydrogen arsenate, HAsO_4^{--}	
Metarsenate, AsO_3^-	Metarsenite, AsO_2^-
Pyroarsenate, $\text{As}_2\text{O}_7^{---}$	

In solution, all the various arsenates tend to go over into orthoarsenate, AsO_4^{---} ; and the metarsenite seems to be in ready equilibrium with the orthoarsenite. In practice, therefore, only two anions need to be considered: AsO_4^{---} and AsO_3^{---} . Most of the solid arsenites are metarsenites.

Arsenate

The Acid.— H_3AsO_4 is a white solid, sparingly soluble in water. It is a moderately strong acid, slightly weaker than H_3PO_4 . The constant for its primary ionization is 5×10^{-3} .

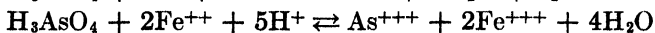
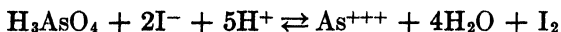
Solubilities.—The arsenates of Na^+ , K^+ , and NH_4^+ are soluble in water; all others require acids to bring them into solution.

Reactions.—The most important analytical reactions of AsO_4^{---} are given below.

Precipitation.—With AgNO_3 solution, AsO_4^{---} gives a chocolate precipitate of Ag_3AsO_4 , soluble in HNO_3 or NH_4OH ; with "magnesia mixture," a white precipitate of $\text{MgNH}_4\text{AsO}_4$ (cf. MgNH_4PO_4), soluble in strong acids; and with $(\text{NH}_4)_2\text{MoO}_4 + \text{HNO}_3$, yellow $(\text{NH}_4)_3\text{AsO}_4 \cdot 12\text{MoO}_3$, forming slowly. All of these reactions are exactly parallel to those of PO_4^{---} .

With H_2S , AsO_4^{---} gives precipitates of As_2S_5 or $\text{As}_2\text{S}_3 + 2\text{S}$, depending upon the conditions. In cold solutions containing an excess of HCl , As_2S_5 is the main product. If the solution contains a small amount of HCl or if it is hot, the precipitate consists of $\text{As}_2\text{S}_3 + 2\text{S}$, mixed with some As_2S_5 (see page 210).

Reduction.— AsO_4^{---} in acid solution is reduced by strong reducing agents.



These reactions are reversible; but the first may be made to go to completion by removing the I_2 by $\text{S}_2\text{O}_3^{--}$; and the second becomes complete in the presence of excess Cl^- , when the volatile AsCl_3 is distilled out.

Arsenite

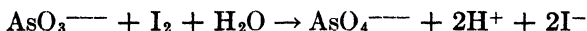
The Acid.—Free arsenious acid has not been isolated; the anhydride, As_2O_3 , is slightly soluble in water, giving what may be considered a dilute solution of H_3AsO_3 . It is readily soluble in NaOH or KOH , forming arsenites. Arsenious acid is much weaker than arsenic acid, with K_1 being 6×10^{-10} .

Solubilities.—The arsenites of Na^+ , K^+ , and NH_4^+ are soluble in water; the others require acids for their solution (*cf.* arsenates).

Precipitation.—With Ag^+ , AsO_3^{--} forms yellow Ag_3AsO_3 , soluble in dilute HNO_3 or NH_4OH ; with "magnesia mixture," no reaction occurs; and with $(\text{NH}_4)_2\text{MoO}_4 + \text{HNO}_3$, no reaction except as the AsO_3^{--} is oxidized to AsO_4^{--} .

H_2S precipitates As_2S_3 promptly from AsO_3^{--} in acid solution; in alkaline solution, soluble AsS_3^{--} is formed (see page 209).

Oxidation.— AsO_3^{--} is readily oxidized to AsO_4^{--} if the solution is not too acid. In solutions buffered by NaHCO_3 (practically neutral), AsO_3^{--} is oxidized by I_2 .



Detection.—The detection of AsO_4^{--} and AsO_3^{--} is based upon (1) the detection of arsenic during the cation analysis; (2) the colors of the Ag^+ salts; (3) the general nature of the unknown. For example: The analysis of a simple salt shows the presence of sodium and arsenic, but no other anion. The salt is therefore one of the sodium arsenates or arsenites.

Distinction between Arsenate and Arsenite.— AsO_4^{--} may be distinguished from AsO_3^{--} by (1) the color of the Ag^+ salt, (2) the speed of precipitation by H_2S , (3) the reaction with I_2 and I^- .

Distinction between As^{+++} and AsO_3^{--} .—The question comes up, When trivalent arsenic is detected, is it present as AsO_3^{--} or As^{+++} ? In view of the weakness of H_3AsO_3 , it is to be expected that water solutions of arsenites should be alkaline in reaction.

If the solution is acid, the arsenic may be assumed to be present as As^{+++} ; for $\text{AsO}_3^{---} + 6\text{H}^+ \rightleftharpoons \text{As}^{+++} + 3\text{H}_2\text{O}$.

CHROMATE AND DICHROMATE

Hexavalent chromium is definitely acidic in nature, forming two well-known series of anions, *viz.*: chromate, CrO_4^{--} ; and dichromate, $\text{Cr}_2\text{O}_7^{--}$. In addition to these, there is evidence of the existence of other Cr^{VI} anions, such as HCrO_4^- and possibly HCr_2O_7^- . Since only chromates and dichromates have been separated in the solid state, the discussion will be limited largely to them.

The CrO_4^{--} ion is lemon yellow in color. From this it might be expected that the solid chromates formed with colorless cations would be yellow. Such is usually the case, though there are several exceptions; *e.g.*, Ag_2CrO_4 and HgCrO_4 are bright red. Most solid dichromates are orange, though bismuthyl dichromate, $(\text{BiO})_2\text{Cr}_2\text{O}_7$, and zinc dichromate, ZnCr_2O_7 , are more yellow than orange.

A number of the chromates have important industrial uses. Lead chromate is used as a yellow pigment in paints. The sodium, potassium, and ammonium salts are used in the manufacture of dyes and inks, in the tanning of leather, and in chromium plating.

The Acid.—When chromic anhydride, CrO_3 , is dissolved in water, an orange-red solution is obtained which appears to contain both monochromic and dichromic acids, H_2CrO_4 and $\text{H}_2\text{Cr}_2\text{O}_7$. Neither of these acids has been isolated in the dry state; for, upon evaporation of the solvent, decomposition occurs, leaving a residue of CrO_3 . Still the solution is referred to as *chromic acid*, and its formula in equations written H_2CrO_4 , regardless of the presence of $\text{H}_2\text{Cr}_2\text{O}_7$.

Chromic acid is a strong acid, its primary ionization approximating 100 per cent in dilute solution (*cf.* H_2SO_4). The most important property is its oxidizing action. The "cleaning solution" of the laboratory is a solution of CrO_3 in concentrated H_2SO_4 , generally prepared by mixing solid $\text{Na}_2\text{Cr}_2\text{O}_7$ or $\text{K}_2\text{Cr}_2\text{O}_7$ with concentrated H_2SO_4 .

Solubilities.—The chromates soluble in water are Na_2CrO_4 , K_2CrO_4 , $(\text{NH}_4)_2\text{CrO}_4$, MgCrO_4 , CaCrO_4 , and CuCrO_4 . The

other chromates are soluble in strong acids, with the exception of *fused* PbCrO_4 . Among the insoluble dichromates are $(\text{BiO})_2\text{Cr}_2\text{O}_7$, CuCr_2O_7 , $\text{Ag}_2\text{Cr}_2\text{O}_7$, etc.

The Chromate-dichromate Equilibrium.—When a $\text{Cr}_2\text{O}_7^{--}$ solution is diluted, the orange color of the $\text{Cr}_2\text{O}_7^{--}$ is gradually displaced by the yellow color of the CrO_4^{--} ion. And when a CrO_4^{--} solution is acidified, the yellow CrO_4^{--} seems to disappear in favor of the orange $\text{Cr}_2\text{O}_7^{--}$. These changes are usually represented by the equilibrium $\text{Cr}_2\text{O}_7^{--}$ (orange) + $\text{H}_2\text{O} \rightleftharpoons 2\text{CrO}_4^{--}$ (yellow) + 2H^+ . More careful study of the problem indicates that the case is not so simple. The hydrogen chromate ion HCrO_4^- seems to be present also, apparently in considerable amount. So the equilibrium is better represented:



The equilibriums involved in the chromic acid system have been extensively studied without decisive results, for different methods give different values for the dissociation constants. The following values by Sherrill are representative:

$$K_1 = \frac{[\text{H}^+][\text{HCrO}_4^-]}{[\text{H}_2\text{CrO}_4]} = 1, \text{ approx.}$$

$$K_2 = \frac{[\text{H}^+][\text{CrO}_4^{--}]}{[\text{HCrO}_4^-]} = 8.4 \times 10^{-7}$$

$$K_3 = \frac{[\text{HCrO}_4^-]^2}{[\text{Cr}_2\text{O}_7^{--}]} = 0.013$$

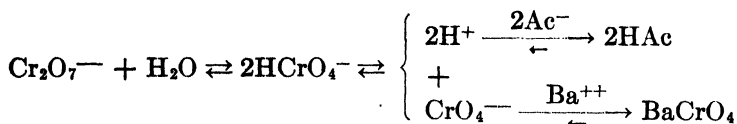
The value for K_1 , the primary ionization constant, shows that H_2CrO_4 is a strong electrolyte, belonging to the "completely ionized" group. K_2 is surprising small, indicating a very high stability for the HCrO_4^- —approximately that of the H_2CO_3 molecule or the HSO_3^- ion. K_3 indicates that the concentration of the $\text{Cr}_2\text{O}_7^{--}$ ion must also be very low, except in the case of concentrated chromic acid. It therefore follows that CrO_4^{--} ions disappear very rapidly from a solution as the concentration of H^+ ions is increased, without any corresponding increase in the $\text{Cr}_2\text{O}_7^{--}$ concentration.

This explains why Pb^{++} is precipitated by $\text{K}_2\text{Cr}_2\text{O}_7$ solution as PbCrO_4 and not as PbCr_2O_7 . Both precipitates are insoluble, with solubility products of approximately the same value. But

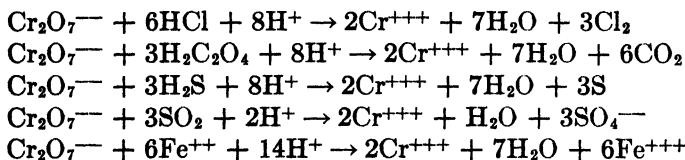
in neutral, or even slightly acid, solution, the $\text{Cr}_2\text{O}_7^{--}$ concentration is very small. Upon addition of a strong acid, such as HNO_3 , the CrO_4^{--} ions are converted into HCrO_4^- without an appreciable increase in the $\text{Cr}_2\text{O}_7^{--}$ concentration, and so solution occurs.

Reactions.—The following reactions are of analytical importance.

1. *Precipitation of Chromate (or Dichromate) Ion.*—The CrO_4^{--} and $\text{Cr}_2\text{O}_7^{--}$ ions are usually precipitated as PbCrO_4 and BaCrO_4 , for these chromates have the lowest solubility in water and in acids. In the presence of a buffer (e.g., $\text{C}_2\text{H}_3\text{O}_2^-$), $\text{Cr}_2\text{O}_7^{--}$ may be quantitatively thrown down by these ions.



2. *Oxidizing Action.*—Chromates in acid medium are strong oxidizing agents and are readily reduced to the Cr^{+++} form. The following equations are representative:



In alkaline solution, the CrO_4^{--} ion is reduced with difficulty, showing that it is a feeble oxidizing agent in comparison to $\text{H}_2\text{Cr}_2\text{O}_7$ (or HCrO_4^- , or $\text{Cr}_2\text{O}_7^{--}$). The reduction product is generally $\text{Cr}(\text{OH})_3$. For example:



This reaction is slow and incomplete. Much of the CrO_4^{--} escapes reduction and is precipitated as brown chromic chromate, $\text{Cr}_2(\text{CrO}_4)_3$.

3. *Chromyl Chloride.*—See page 323.

4. *Reaction with Hydrogen Peroxide.*—See page 248.

Detection.—The detection of CrO_4^{--} and $\text{Cr}_2\text{O}_7^{--}$ is based upon the following reactions: (1) In the solid state, chromates

are yellow, orange, red, or brown and give with acids orange solutions, provided that no reducing agents are present. This effect may be obscured by the presence of other colored materials. (2) During the precipitation of Group II of the cations, this orange color changes to green, and a white precipitate of free sulfur separates. This is followed by the detection of Cr^{+++} in Group III. (3) Acid solution of chromates and dichromates gives with H_2O_2 an unstable blue liquid, soluble in ether. Heat and reducing agents interfere. (4) Yellow precipitates with Pb^{++} and Ba^{++} , insoluble in $\text{HC}_2\text{H}_3\text{O}_2$, are presumptive, but not conclusive, tests.

Chromate or Dichromate?—The question of whether a material contains a chromate or a dichromate must be decided upon such considerations as the following: (1) Chromates soluble in water give yellow solutions, whereas dichromates give orange solutions. (2) Aqueous solutions of dichromates show an acid reaction with litmus and certain other indicators. Chromate solutions are practically neutral. (3) Frequently the formula may be inferred from such considerations as (a) the metallic ions present, (b) color, and (c) solubility. For example, a solid that is deep red in color and soluble in dilute HNO_3 , giving an orange solution containing Ag^+ , is probably Ag_2CrO_4 . Again, a yellow powder containing bismuth is probably $(\text{BiO})_2\text{Cr}_2\text{O}_7$.

SPECIAL ANALYTICAL PROCEDURES

Interferences in the Evolution-of- CO_2 Test for Carbonate.—Excessive boiling should be avoided in making the $\text{Ca}(\text{OH})_2$ test for CO_2 for carbonates. Enough H_3BO_3 from BO_3^- may distill over to form white $\text{Ca}(\text{BO}_2)_2$; and the anions of the volatile acids of Group I, II, and IV may come over in sufficient amount actually to neutralize the $\text{Ca}(\text{OH})_2$. Persistent boiling may even carry over enough H_2SO_4 in the spray to form a precipitate of CaSO_4 .

Carbonate in the Presence of Sulfite and Thiosulfate.—Upon acidification, SO_3^- and S_2O_3^- evolve SO_2 , which sometimes forms a precipitate of CaSO_3 with $\text{Ca}(\text{OH})_2$. This complication may be obviated by adding a little H_2O_2 to the solution. KMnO_4 should not be used, for it evolves CO_2 from oxalates.

Separation of Carbonate from Oxalate.—Carbonates are decomposed upon mere acidification; oxalates and tartrates

require the presence of an oxidizing agent. Hence, CO_3^{--} may be separated by adding a nonoxidizing acid (*e.g.*, dilute H_2SO_4) and boiling until the CO_2 is completely expelled.

Oxidizing agents may, in some cases, be present in the material to be tested for $\text{C}_2\text{O}_4^{--}$; *e.g.*, a mixture of CaCO_3 , CaC_2O_4 , and MnO_2 . In this case, the interfering action of the MnO_2 may be obviated by extracting the CaCO_3 by $\text{HC}_2\text{H}_3\text{O}_2$. In all such cases, the oxalate should be protected from oxidation by the addition of Ca^{++} to convert it into its most insoluble form, *viz.*, CaC_2O_4 .

Separation of Carbonate, Oxalate and Tartrate.—The carbonate is first removed by acidification with $\text{HC}_2\text{H}_3\text{O}_2$ and boiling until the reaction is complete. $\text{NaC}_2\text{H}_3\text{O}_2$ and CaCl_2 are then added, precipitating CaC_2O_4 and leaving $\text{C}_4\text{H}_4\text{O}_6^{--}$ in solution.

Separation of Sulfite from Thiosulfate.— SO_3^{--} ions are slowly precipitated by $\text{Sr}(\text{NO}_3)_2$, giving SrSO_3 . Usually 10 or 12 hr. is required for a complete separation of the SO_3^{--} . This precipitate may consist of other substances—*e.g.*, SrC_2O_4 or SrSO_4 —and the presence of SO_3 should be confirmed by the proper test. The test for $\text{S}_2\text{O}_3^{--}$ in the filtrate is carried out in the usual way.

Sulfite and Thiosulfate in the Presence of Sulfide.— S^{--} ions interfere with the tests for both SO_3^{--} and $\text{S}_2\text{O}_3^{--}$ by forming H_2S upon acidification, and this product reacts with SO_2 , giving a precipitate of sulfur, thus: $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$. Usually, SO_3^{--} in the presence of S^{--} gives the reactions of $\text{S}_2\text{O}_3^{--}$. The best method for separating S^{--} ions from SO_3^{--} and $\text{S}_2\text{O}_3^{--}$ is by shaking with a suspension of CdCO_3 : $\text{S}^{--} + \text{CdCO}_3 \rightarrow \text{CdS} + \text{CO}_3^{--}$. The procedure of precipitation of all three ions as Ag^+ precipitates, followed by the extraction of Ag_2SO_3 and $\text{Ag}_2\text{S}_2\text{O}_3$ by means of HNO_3 is not satisfactory, owing to the instability of $\text{Ag}_2\text{S}_2\text{O}_3$.

Nonprecipitation of Silver and Barium Borates.—Frequently the reagents of Anion Group III give no indication of the presence of the BO_3^{--} ion. This is owing to a relatively high solubility of AgBO_2 and $\text{Ba}(\text{BO}_2)_2$, particularly in the presence of NH_4^+ ions. Hence it is advisable to make tests for BO_3^{--} on all general unknowns, just as though BO_3^{--} belonged to Anion Group IV.

Borate in the Presence of Copper or Barium.— Cu^{++} and Ba^{++} ions interfere with the flame test for BO_3^- by giving green flames. These interfering ions are removed by the general method of precipitation with Na_2CO_3 . The filtrate is acidified with dilute H_2SO_4 , and then the flame test is made in the regular way.

Interferences with the Turmeric Test.—Besides the charring effect of free H_2SO_4 , a number of reagents interfere with the turmeric test by giving a brown color to the paper upon drying. These interfering materials, *e.g.*, zirconate and tantalate, are, for the most part, uncommon. The most common interfering ion is molybdate, MoO_4^- .

Interferences with the Phosphate Test.—The precipitation of $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ is subject to the following interferences: (1) A large excess of Cl^- interferes, possibly by interaction with the MoO_3 factor. This Cl^- may be removed by adding an excess of HNO_3 and evaporating. (2) Reducing agents interfere, owing to the reduction of the MoO_3 . These should be removed by appropriate reactions. (3) Ferrocyanides form with MoO_4^- ions a dark-brown precipitate, insoluble in dilute mineral acids.

Distinction between Arsenate and Arsenite.—The form of arsenic at the time of its detection in Cation Group II gives no basis for deciding whether the element was present in the original in the trivalent or the pentavalent condition. The HNO_3 procedure for regulating acidity converts it into the AsO_4^- form in all cases. In addition to (1) the colors of the Ag^+ salts and (2) the reactions with I_2 and I^- , the general nature of the original material should be considered. In the presence of reducing agents, the element is presumably present as AsO_3^- and in the presence of oxidizing agents, as AsO_4^- .

AsO_3^- ions may be separated from AsO_4^- (and PO_4^-) ions by precipitating the latter as $\text{MgNH}_4\text{AsO}_4$ by means of magnesia mixture. The AsO_3^- in the filtrate may be detected by the precipitation of As_2S_3 from a solution in concentrated HCl by H_2S .

Separation of Phosphate and Arsenate.—The AsO_4^- ion gives all the reactions of the PO_4^- ion and must therefore be separated before testing for the latter. This separation is effected by the precipitation of As_2S_3 by means of H_2S . The use of I^-

ions as a catalyst is not recommended, since they react with the molybdate reagent, giving a blue color. The approved method is as follows.

Evaporate the solution almost to dryness, and take up the residue in concentrated HCl. Saturate the hot solution with H_2S , shaking the flask occasionally. After precipitation is complete (shown by test on the filtrate), evaporate the solution to a small volume. Add an equal volume of concentrated HNO_3 and evaporate almost to dryness. Take up the residue in dilute HNO_3 , and test it for PO_4^{3-} in the usual way, using the $(\text{NH}_4)_2\text{MoO}_4\text{-HNO}_3$ reagent.

Interferences in the Test for Chromate.—Iodide ions interfere with the H_2O_2 test for CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ by forming free I_2 , which colors the ether brown-red. The presence of I^- is strongly indicative of the absence of chromates, which are readily reduced by I^- ions. However, these interfering ions can be removed by AgNO_3 , and the test for chromate made on the filtrate.

Certain cations interfere, especially in the presence of concentrated HCl. Co^{++} salts tend to give the ether a blue color, and Cu^{++} and Fe^{+++} a yellow-brown color. These cations may be removed by Na_2CO_3 .

Exercises

1. In the equilibrium $\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{Ca}(\text{HCO}_3)_2$, what would be the effect of adding the following: $\text{Ca}(\text{OH})_2$, heat, pressure, NaHCO_3 solution, NH_4OH , $\text{HC}_2\text{H}_3\text{O}_2$?
2. Consult the Solubility Table, and suggest an anion that, if present in large quantity, might give a pseudo test for CO_3^{2-} .
3. Name five anions that are given to complex formation—*e.g.*, $\text{AgCN} + \text{CN}^- \rightarrow \text{Ag}(\text{CN})_2^-$.
4. A solution of Na_2CO_3 is slowly saturated with SO_2 . Write ionic equations for the reactions involved in the order of their occurrence.
5. Consult the Solubility Table, and suggest cations that might be used to separate (a) CrO_4^{2-} and AsO_4^{3-} , (b) BO_3^{3-} and $\text{S}_2\text{O}_3^{2-}$, (c) $\text{C}_2\text{O}_4^{2-}$ and $\text{C}_4\text{H}_4\text{O}_6^{2-}$.
6. Suggest a mixture, containing no carbonate but yet giving off CO_2 upon acidification.
7. How would you make the following tests? (a) CO_3^{2-} and HCO_3^- in the presence of both. (b) SO_3^{2-} and HSO_3^- in the presence of both. (c) SO_3^{2-} and $\text{S}_2\text{O}_3^{2-}$ in the presence of both.
8. Calculate from appropriate constants whether ZnS and MnS would be soluble in 0.1 molar solutions of $\text{H}_2\text{C}_2\text{O}_4$.
9. Write equations for the ignition of BaC_2O_4 , $\text{Ag}_2\text{C}_2\text{O}_4$, and HgC_2O_4 .
10. CaC_2O_4 is soluble in HCl but not in $\text{HC}_2\text{H}_3\text{O}_2$. Explain in non-mathematical terms.

11. Would you expect the flame test for BO_3^{---} to be as successful on $\text{Ca}_2\text{B}_6\text{O}_{11}$ as on $\text{Na}_2\text{B}_4\text{O}_7$? Explain your answer.

12. What volume of 0.1 *M* KMnO_4 would be necessary to oxidize 1.46 g. of CaC_2O_4 in the presence of dilute H_2SO_4 ?

13. To 0.12 mole of K_3AsO_4 are added excess of KI and dilute H_2SO_4 . How many cubic centimeters of 0.3 *M* $\text{Na}_2\text{S}_2\text{O}_3$ would be needed to decolorize the mixture?

14. How many grams of Na_2SO_3 (mol. wt., 125) would be needed to decolorize 12 cc. of 0.3 *M* KMnO_4 in the presence of dilute H_2SO_4 ?

15. What weight of $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 3\text{H}_2\text{O}$ would be formed from 0.358 g. of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$?

16. The solubility of AgBO_2 (100 per cent ionized) in water is 0.06 mole per liter. Calculate (a) its solubility product and (b) its solubility in 0.1 *M* AgNO_3 (90 per cent ionized).

17. What volume of 0.1 *M* KMnO_4 is necessary to oxidize 0.378 g. of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$?

18. What weight of chrome alun, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, can be formed by saturating a solution of $\text{K}_2\text{Cr}_2\text{O}_7$ with SO_2 and evaporating the product?

19. What volume of 0.5 *M* $\text{Na}_2\text{S}_2\text{O}_3$ must be added to 48 cc. of 0.1 *M* KMnO_4 in the presence of dilute H_2SO_4 to decolorize the mixture?

20. Try to devise a procedure for detecting the anion groups in the solid mixture $\text{CaCO}_3 + \text{CaC}_2\text{O}_4 + \text{CaC}_2\text{H}_3\text{O}_2$.

21. Identify the following anions of Group III:

(a) A colorless anion that gives with Ca^{++} a white precipitate, insoluble in dilute $\text{HC}_2\text{H}_3\text{O}_2$.

(b) An anion whose Ag^+ salt is yellow and whose acid solution gives a yellow precipitate with H_2S .

(c) An anion forming a white Ag^+ salt, turning brown (not black) upon the addition of excess water.

(d) An anion that decolorizes acidified KMnO_4 solution with the evolution of CO_2 but that does not form a silver mirror with $\text{Ag}(\text{NH}_3)_2^+$.

(e) An anion that gives no reaction with magnesia mixture but a yellow precipitate upon warming with $(\text{NH}_4)_2\text{MoO}_4 + \text{HNO}_3$.

CHAPTER XXIII

ANION GROUP IV

This group contains those anions whose Ag^+ and Ba^{++} salts are soluble in water.

Nitrate, NO_3^-	Persulfate, $\text{S}_2\text{O}_8^{--}$
Chlorate, ClO_3^-	Nitrite, NO_2^-
Perchlorate, ClO_4^-	Acetate, $\text{C}_2\text{H}_3\text{O}_2^-$
Permanganate, MnO_4^-	

Owing to the appreciable solubility of their Ag^+ salts, the presence of NO_2^- and $\text{C}_2\text{H}_3\text{O}_2^-$ may not be indicated in Anion Group II. They are therefore repeated in this group.

It should be noted that the reagents for the anion groups [*i.e.*, AgNO_3 and $\text{Ba}(\text{NO}_3)_2$] give no indication of the presence of the anions of Group IV. Hence the ions of this group should be tested for in all cases.

NITRATE

The univalent nitrate ion NO_3^- is the most important derivative of pentavalent nitrogen.

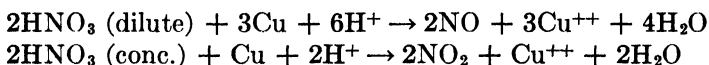
The Acid.—The 68 per cent HNO_3 of commerce is a clear liquid, boiling at 120.5° . On exposure to light, it undergoes slight decomposition: $4\text{HNO}_3 \rightarrow 2\text{H}_2\text{O} + 4\text{NO}_2 + \text{O}_2$. The NO_2 dissolves in the acid, giving it a yellow color. Nitric acid is a strong acid, of about the same ionization as HCl . It is more stable than nitrous acid, HNO_2 ; dilute HNO_3 does not give off a perceptible amount of colored fumes, even upon boiling.

Solubilities.—All the nitrates are soluble. A few basic nitrates (*e.g.*, BiONO_3) are insoluble in water but dissolve in dilute HNO_3 .

Oxidizing Action.—Contrary to popular opinion, HNO_3 is not one of the strongest oxidizing agents. It is much weaker than PbO_2 or MnO_2 in acid solution. For example, Mn^{++} is oxidized to MnO_4^- by $\text{PbO}_2 + \text{HNO}_3$, whereas HNO_3 alone is without effect.

One of the most interesting questions is, Is the NO_3^- ion an oxidizing agent? Nitrates are very difficult to reduce, except in acid solution. This is hard to interpret except upon the assumption that the HNO_3 molecule, and not the NO_3^- ion, is the actual oxidizing agent. The statement that "the reduction of nitrates is catalyzed by the presence of H^+ ions" is merely a statement of fact and not a description of the mechanism. A satisfactory answer to the question is not forthcoming.

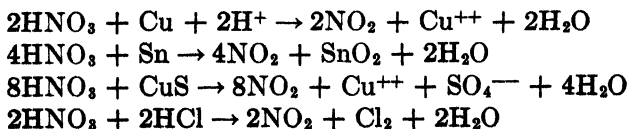
Reduction Products of Dilute and Concentrated Nitric Acid.—When a reducing agent reacts with ordinary dilute HNO_3 , the reduction product is nitric oxide, NO ; with concentrated HNO_3 , nitrogen dioxide, NO_2 . To illustrate:



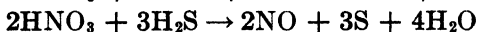
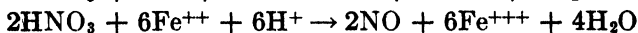
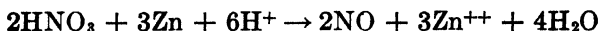
It does not follow that dilute HNO_3 is three times as good an oxidizing agent as concentrated HNO_3 , just because it oxidizes three times as much copper. The vigor of the reactions is determined by the energy contents of different concentrations of the acid and not by the reduction products. Very probably, there are intermediate reactions in both cases—possibly with the same initial reduction product. Assume that this initial reduction product is NO_2 . Now NO_2 reacts reversibly with water to form NO : $3\text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{HNO}_3 + \text{NO}$. That is, if NO_2 were formed in dilute solution, it would be changed to NO by the excess of water present. On the other hand, if NO were the primary product in concentrated HNO_3 solution, it would be oxidized to NO_2 by the HNO_3 before it could escape from the solution. The oxidizing strength of HNO_3 therefore increases with its concentration, just as would be expected.

The following equations exemplify the general behavior of HNO_3 as an oxidizing agent.

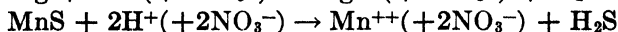
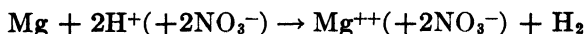
With concentrated HNO_3 ,



With dilute HNO_3 ,



With very dilute HNO_3 , the oxidizing action of the acid disappears.

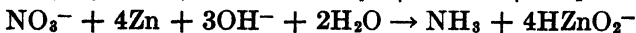
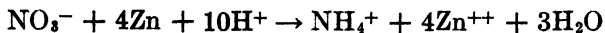


This behavior is easily explained by assuming that very dilute HNO_3 is completely ionized and contains H^+ and NO_3^- ions but no HNO_3 molecules. It therefore behaves like the nonoxidizing acids, such as HCl and dilute H_2SO_4 .

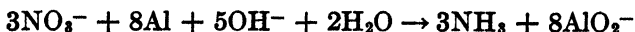
Reaction with Ferrous Sulfate.—If concentrated HNO_3 is introduced below a solution of FeSO_4 , a brown layer or ring is formed at the junction of the two liquids. The NO , formed by the reduction of HNO_3 by Fe^{++} , unites with the excess of FeSO_4 , forms a brown compound of the approximate formula $\text{FeSO}_4 \cdot \text{NO}$. This reaction does not take place if dilute HNO_3 is used, because it is not a strong enough oxidizing agent to react with the FeSO_4 .

Nitrous acid (or an acidified solution of a nitrite) gives this brown solution with FeSO_4 .

Reduction of the Nitrate Ion to Ammonia.—Very active reducing agents, such as zinc, reduce NO_3^- to NH_3 . This reaction takes place to some extent in acid medium but much better in alkaline medium.



The vigor of this reaction is attributed to the high overvoltage (see page 250) of zinc. Aluminum in the presence of NaOH also reduces NO_3^- to NH_3 .



No NH_3 is formed by reduction with aluminum in acid medium.

Detection.—The nitrate ion, as such, has no characteristic behavior that can be used in its identification. The best that can be done is to break it down into one of its reduction products which will show a conspicuous behavior.

1. *Formation of Brown NO₂.*—Nitric acid is too stable to give off brown fumes of NO₂ upon boiling. Hence, no colored gas is evolved upon acidification of a NO₃⁻ solution by H₂SO₄ (cf. Nitrite, page 348). Upon the addition of copper turnings, NO and NO₂ are formed by reduction of the HNO₃. This test is not highly sensitive.

2. *Brown-ring Test.*—Ferrous sulfate, FeSO₄, is added to the solution to be tested, and concentrated H₂SO₄ is introduced beneath the mixture. At the junction, brown FeSO₄·NO is formed. The brown liquid is decomposed upon warming, so that the test must be applied to cold solutions.

There are several interferences with this test: Nitrite, NO₂⁻, interferes by coloring the whole mixture brown; I⁻ is oxidized by the concentrated H₂SO₄, forming a brown ring of I₂. CrO₄⁻ and Cr₂O₇⁻ are reduced to Cr⁺⁺⁺, giving a greenish ring. ClO₃⁻ is decomposed by H₂SO₄, forming ClO₂, which forms with H₂SO₄ a yellow-brown solution. These interferences may be removed as follows: I⁻, CrO₄⁻, and Cr₂O₇⁻ by AgClO₄ or Ag₂SO₄ in *neutral* solution; and ClO₃⁻ by reduction to Cl⁻ by means of Zn + dilute H₂SO₄.

3. *Reduction to NH₃.*—If the above interferences are present, the NO₃⁻ ion is best detected as follows: Excess NaOH is added and the mixture warmed until all NH₄⁺ is expelled as NH₃. Then zinc dust is added, reducing NO₃⁻ to NH₃, which may be detected by litmus paper. This reaction is also given by NO₂⁻ ions.

4. *Brucine Reaction.*—The NO₃⁻ anion reacts with a solution of brucine in concentrated H₂SO₄, forming a red coloration, which changes through orange to yellow and finally to greenish yellow. Nitrites form enough HNO₃ upon acidification with H₂SO₄ to give this test.

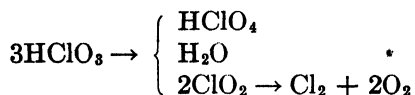
It appears that NO₂⁻ anions interfere with all the tests for NO₃⁻. However, this should cause no worry. Nitrites always contain nitrates. So in the case of the presence of nitrite, without any test being made, NO₃⁻ may be assumed to be present.

CHLORATE

Chlorates, on account of their explosiveness, are found in very few industrial materials. Fireworks, matches, and certain

explosives are representative of the commercial products in which chlorates do appear.

The Acid.—Chloric acid, HClO_3 , is a colorless liquid. It is very unstable, decomposing into perchloric acid, chlorine, and oxygen.

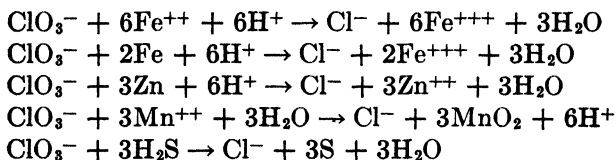


When concentrated acids, such as H_2SO_4 and HCl , are added to solid chlorates, violent explosions may occur. The explosive ingredient seems to be the chlorine dioxide, ClO_2 . When small amounts of chlorate are used, the ClO_2 dissolves in the concentrated H_2SO_4 , forming a yellow solution.

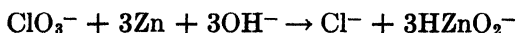
Dilute HClO_3 is a strong acid, about as well ionized as HCl or HNO_3 .

Solubilities.—All chlorates are soluble in water. Potassium chlorate, KClO_3 , is the most insoluble—about 0.7 mole per liter. This solubility is too large for KClO_3 to be used as a separation form.

Oxidizing Action.—Chlorates in acid solution (*i.e.*, HClO_3 solution) are strong oxidizing agents. For example:



In neutral or alkaline mediums, the oxidizing potential is not so great, and more active reducing agents must be used to effect the reduction of ClO_3^- to Cl^- ; *e.g.*,

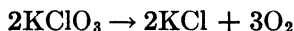


Reduction by Hydrochloric Acid.—The reduction of chlorates by HCl is rather complex. In addition to the formation of ClO_2 by the decomposition of the HClO_3 , a reduction of the ClO_3^- to Cl_2 also occurs.



This reaction is independent of the decomposition of HClO_3 , and the two cannot be combined into a single equation.

Ignition.—Chlorates are decomposed into chlorides upon ignition. The reaction is not a simple one, for perchlorates are formed as intermediate products. For ordinary purposes, the following may be taken as a type equation:



The decomposition proceeds rapidly if the heating is carried out in contact with a reducing agent, such as charcoal: $2\text{KClO}_3 + 3\text{C} \rightarrow 2\text{KCl} + 3\text{CO}_2$. The speed of the reaction is also increased by the presence of MnO_2 , which acts catalytically.

Reaction with Aniline Sulfate.—A small amount of chlorate dissolved in cold concentrated H_2SO_4 gives with aniline sulfate solution a deep blue color. This reaction seems specific for ClO_2 and consequently is not given by NO_3^- .

Indigo Test.—Solutions of indigo in H_2SO_4 are bleached by ClO_3^- in the presence of SO_2 . Possibly the H_2SO_3 reduces ClO_3^- to Cl_2 , which oxidizes indigo to a colorless form. Nitrates give the same reaction.

Detection.—The following reactions are used in the detection of ClO_3^- : (1) Small particles of chlorate form a yellow color with cold concentrated H_2SO_4 . NO_3^- , NO_2^- , Br^- , I^- , $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{CN})_6^{3-}$, organic matter, etc., interfere by giving colors. This yellow solution gives a blue color with aniline sulfate. (2) A more reliable procedure is to reduce the ClO_3^- to Cl^- by means of zinc in dilute H_2SO_4 solution and to precipitate the Cl^- as AgCl by AgNO_3 solution. Cl^- and other members of Anion Group I must be removed previously by AgNO_3 . (3) Upon warming with $\text{MnCl}_2\text{-HCl}$ solution, the solution should give a brown color, showing the presence of an oxidizing agent.

PERCHLORATE

The increasing use of perchloric acid as a precipitant for K^+ ions and as a solvent for various materials and of magnesium perchlorate as a drying agent calls for the inclusion of this anion among the common radicals.

The Acid.—The usual commercial form of this acid contains 70 to 73 per cent of pure HClO_4 and boils without decomposition at 203° . The anhydrous form may be obtained by careful distillation with dehydrating agents and is a colorless oily liquid

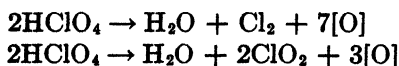
that decomposes upon standing, sometimes with terrific violence.

Perchloric acid is a strong acid, resembling H_2SO_4 in a general way. At ordinary temperatures, the concentrated acid is a weak oxidizing agent; but, upon heating, it becomes comparable in oxidizing strength to $\text{H}_2\text{Cr}_2\text{O}_7$ and even to HMnO_4 . Hot HClO_4 has been found very serviceable in dissolving sulfides (see page 108), alloys, etc. When HClO_4 is cooled and diluted, the oxidizing action almost wholly disappears; *i.e.*, it is extremely difficult to reduce. This may be explained by assuming that the active oxidizing agent is the HClO_4 molecule (or its anhydride, Cl_2O_7). The dilute acid, on the contrary, is a strong acid, containing the acid almost wholly in the form of its ions, and the ClO_4^- ion does not seem to be an oxidizing agent.

Perchloric acid should never be heated with organic substances like alcohols and carbohydrates for explosions of terrific violence may occur. Probably perchloric esters similar to the nitric esters (*e.g.*, nitroglycerin or nitrocellulose) are formed.

Solubilities.—Perchlorates are generally soluble in water. The most insoluble is potassium perchlorate, KClO_4 , which dissolves to the extent of 20.39 g. per liter at 25° . Ammonium perchlorate, NH_4ClO_4 , is considerably more soluble—219.1 g. per liter. However, this difference is not always sufficient to keep it from forming in the test for K^+ in Cation Group V. Hence it is safer previously to remove the NH_4^+ ion by evaporation with HNO_3 . Cadmium forms a rather insoluble cadmium ammonia perchlorate, $\text{Cd}(\text{NH}_3)_4(\text{ClO}_4)_2$, which may be used as a test for either Cd^{++} or ClO_4^- ions.

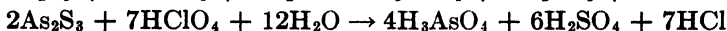
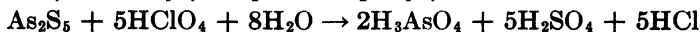
Oxidizing Reactions.—The oxidizing reactions of HClO_4 are complex and hard to interpret. In some cases, the principal reduction products seem to be Cl_2 and ClO_2 , represented by the partial equations



In other cases, the main reduction product seems to be the Cl^- ion.



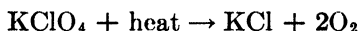
In the solution of sulfur and sulfides, the latter type of reaction seems to predominate.



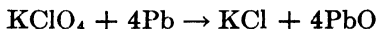
With certain other active reducing agents, $HClO_4$ is reduced more or less quantitatively to the Cl^- ion.



Ignition.—Upon ignition, the alkaline perchlorates are decomposed, forming chlorides; *e.g.*,



This decomposition proceeds more readily in the presence of MnO_2 , which catalyzes the reaction. Upon ignition of perchlorates with certain reducing agents, a similar reduction is effected. In the case of carbon, sulfur, and certain other reducing agents, the reaction may be dangerously explosive. With less active agents, it proceeds smoothly; *e.g.*,



Perchlorates are completely decomposed by heating with an excess of an NH_4^+ salt; *e.g.*,



Detection.—The following reactions are available for testing for the ClO_4^- ion.

1. *The Precipitation of $KClO_4$.*—In solutions that are not too dilute, ClO_4^- is precipitated by K^+ as white $KClO_4$. Anions which form insoluble potassium salts interfere: *e.g.*, fluosilicate, SiF_6^{--} ; fluoborate, BF_4^- ; hydrogen tartrate, $HC_4H_4O_6^-$; picrate, $C_6H_2(NO_2)_3O^-$; etc.

2. *The Reduction of ClO_4^- to Cl^- .*—This is best carried out by the ignition of alkaline perchlorates, preferably in the presence of MnO_2 . The residue is extracted with warm water, and the Cl^- formed is precipitated as $AgCl$. Evidently all the ions of Anion Group I interfere and must be removed previously. ClO_3^- must also be absent, since it is reduced to Cl^- .

3. *Precipitation of $Cd(NH_3)_4(ClO_4)_2$.*—Perchlorate ions give a white crystalline precipitate with a saturated solution of $Cd(NO_3)_2$ in concentrated NH_4OH . All anions which form with Cd^{++} precipitates that are insoluble in NH_4OH interfere— S^- ions, for example.

4. *Precipitation by Organic Substances.*—Several organic compounds (*e.g.*, the alkaloid, strychnine sulfate) have been suggested as precipitants.

PERMANGANATE

The permanganate ion MnO_4^- has already been considered, in a manner, in connection with the manganous ion Mn^{++} . The student should review pages 253 to 255 as supplementary to the present treatment.

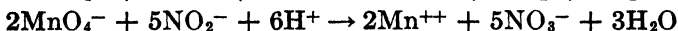
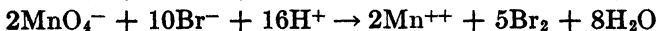
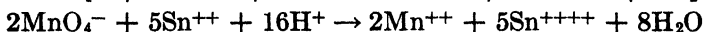
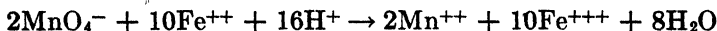
The MnO_4^- anion is formed by treating Mn^{++} or MnO_2 by powerful oxidizing agents. Its purple color is so intense that 1 mg. of MnO_4^- will give a reddish color to 1 l. of solution. The color of the anion is therefore a very sensitive test for Mn^{++} and its derivatives. The most important permanganate, chemically and industrially, is potassium permanganate, formed by heating MnO_2 with KOH-KNO_3 mixture.

The Acid.—Permanganic acid, HMnO_4 , is known only in solution. Upon evaporation, it decomposes into water and the anhydride, Mn_2O_7 , and the latter decomposes explosively into MnO_2 and oxygen.

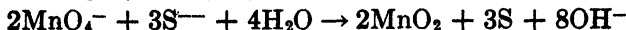
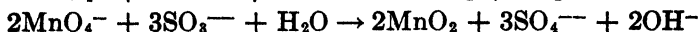
Solubilities.—All permanganates are soluble in water.

Reactions.—See pages 253 to 255 for the formation and general properties of permanganates.

Oxidizing Action.—Permanganates are strong oxidizing agents, but the reduction product varies with the nature of the medium. In acid medium, the reduction product is Mn^{++} and not MnO_2 (unless insufficient acid is present). For example:



In neutral or alkaline medium, the reduction product is a brown-black precipitate of MnO_2 . For example:



See pages 253 to 255 for other oxidation reactions.

The difference in the course of the reaction in acid and alkaline mediums may be attributed to MnO_2 being a strong oxidizing agent in acid medium, but not in alkaline medium. It is possibly an intermediate product in oxidations in acid solution but is used up as fast as it is formed. There is reason to believe that MnO_2 in the presence of H^+ is almost as active an oxidizer as HMnO_4 .

Detection.—The permanganate ion MnO_4^- is detected in the course of cation analysis by the following reactions: (1) A purplish solution, bleached by H_2S in the precipitation of Cation Group II, is followed by the detection of Mn^{++} in Group III. (2) The formation of a brown-black precipitate with MnCl_2 in HCl solution indicates the presence of an oxidizing agent, though not necessarily MnO_4^- . But if MnO_4^- is present, this reaction should be positive. In general, the ion is detected by its purplish-red color.

Care should be taken to distinguish between Mn^{++} and MnO_4^- . It is a blunder of the first magnitude to report Mn^{++} in an unknown when the actual constituent is MnO_4^- .

PERSULFATE

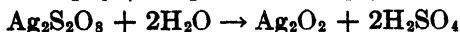
The persulfate anion $\text{S}_2\text{O}_8^{--}$ is increasing in importance by reason of its use as an oxidizing agent in analytical laboratories and in the industries.

The Acid.—Persulfuric acid, $\text{H}_2\text{S}_2\text{O}_8$, is known only in its solution in sulfuric acid. Its most important salt is ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, formed by the electrolysis of ammonium hydrogen sulfate, NH_4HSO_4 .



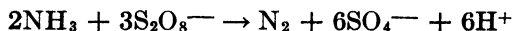
Solubilities.—All persulfates are soluble. Potassium persulfate, $\text{K}_2\text{S}_2\text{O}_8$, seems to be the least soluble, with a solubility of 17.6 g. per liter at 0° .

Oxidizing Action.—Solutions of persulfates decompose slowly in the cold and rapidly upon warming, forming oxygen (or a peroxide) and sulfates. For example:



They are powerful oxidizing agents. In alkaline medium, Mn^{++} is oxidized to MnO_2 , Pb^{++} to PbO_2 , Co^{++} to $\text{Co}(\text{OH})_3$, Ni^{++} to

NiO_2 , and Cr^{+++} to CrO_4^- . In acid solution, Fe^{++} is oxidized to Fe^{+++} , Mn^{++} to MnO_2 , Ag^+ to Ag_2O_2 , and halide ions to free halogens (*e.g.*, Cl^- to Cl_2 , etc.). The oxidizing action in acid solution is intensified by the presence of Ag^+ , so that Mn^{++} is oxidized to HMnO_4 , the halogens to halates (*e.g.*, I^- to IO_3^-), and NH_3 to N_2 .



Detection.—Persulfates are detected by: (1) the oxidation of Mn^{++} to MnO_4^- in the presence of Ag^+ as a catalyst; and (2) the oxidation of Ni^{++} to black NiO_2 in alkaline medium.

SPECIAL ANALYTICAL PROCEDURES

There are certain complications to be kept in mind in testing for the anions of Group IV.

Nitrate in the Presence of Nitrite.—There is no easy test for NO_3^- in the presence of NO_2^- . The Griess test for NO_3^- used in water analysis is considered the best, but it is too sensitive for ordinary use and involves organic reagents not familiar to the elementary student. Furthermore, there is no satisfactory method for separating NO_3^- and NO_2^- ions. In both the ignition-with- NH_4^+ and the reduction-with-urea procedures for removing NO_2^- (page 350), some NO_3^- is formed as a by-product.

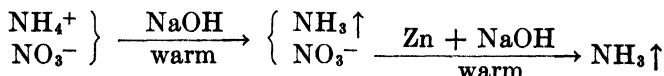
From a different point of view, no test for NO_3^- in the presence of NO_2^- is really required, for all nitrites contain nitrates. In the manufacture of nitrites by reducing nitrates with lead, some nitrate is always left unreduced. And in making nitrites from the oxides of nitrogen, some nitrate is formed, for there is always more NO_2 than NO in the gaseous mixture. Possibly nitrites are oxidized to nitrates to some extent by the air. In short, when NO_2^- is detected, the presence of NO_3^- may be presumed without making a test.

Interferences with the Brown-ring Test.—As stated before, there are many interferences with the brown-ring test. In addition to NO_2^- , the following should be mentioned: I^- , CrO_4^- and $\text{Cr}_2\text{O}_7^{--}$, ClO_3^- , and cations forming insoluble sulfates (Pb^{++} , Ba^{++} , Sr^{++} , and Ca^{++}). Highly colored ions may also mask the reaction. These interferences may be met as follows: I^-

may be removed by Ag_2SO_4 or AgClO_4 in either acid or neutral solution. CrO_4^{--} and $\text{Cr}_2\text{O}_7^{--}$ may be removed by the same Ag^+ solutions, but the solution must be neutral. Cations forming insoluble sulfates and colored cations may be removed by Na_2CO_3 in the usual way.

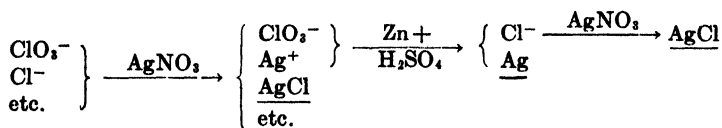
Anions forming gases upon acidification interfere with the brown-ring test and must be previously removed by careful acidification with dilute H_2SO_4 .

Nitrate in the Presence of Ammonium.—When the material contains any of the ions that interfere with the brown-ring test, the analyst usually turns to the evolution-of- NH_3 test, using zinc dust in strongly alkaline medium. Here the principal interference is NH_4^+ . This complication is easily obviated by not adding the zinc until NH_4^+ is completely expelled.



The NH_3 gas is detected by moist litmus paper.

Chlorate in the Presence of Halide Ions.—The best test for ClO_3^- involves its reduction to Cl^- , which is detected by precipitation as AgCl . Cl^- , Br^- , and I^- must previously be removed by AgNO_3 in solutions acidified with HNO_3 . Zinc in the presence of dilute H_2SO_4 is used as the reducing agent. The procedure may be outlined thus:

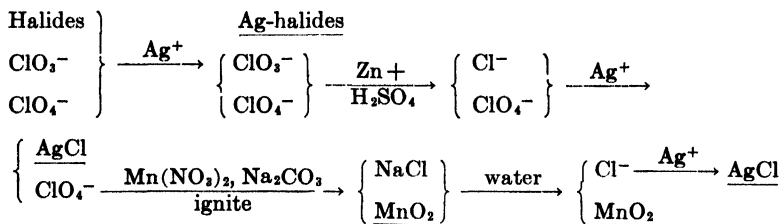


The alkaline solution left after the evolution-of- NH_3 test for NO_3^- may be used in this test for ClO_3^- . However, halide ions must have previously been removed from the original solution by means of Ag_2SO_4 . AgNO_3 cannot be used for the purpose, since this reagent would vitiate the test for NO_3^- .

1. In the removal of the halide ions from a ClO_3^- solution, the solution must not be made too strongly acid, for ClO_3^- may be thus destroyed, particularly by I^- .

2. Na_2SO_3 or NaHSO_3 can be used instead of metallic zinc to reduce ClO_3^- to Cl^- .

Perchlorate in the Presence of Chlorate and the Halides.—In this combination, the halide ions, after their detection in the usual way, are removed by an Ag^+ solution. The ClO_3^- is then reduced to Cl^- by zinc or a sulfite and removed as AgCl . The ClO_4^- is almost unaffected by these reagents. The filtrate from the AgCl precipitate is concentrated to a small volume and made slightly alkaline with Na_2CO_3 . A little $\text{Mn}(\text{NO}_3)_2$ is added, and the mixture evaporated to dryness and ignited. The ClO_4^- is decomposed, leaving Cl^- , which is detected by AgNO_3 in the usual way.



Upon ignition, $\text{Mn}(\text{NO}_3)_2$ decomposes into MnO_2 , which catalyzes the decomposition of the NaClO_4 : $\text{Mn}(\text{NO}_3)_2 + \text{heat} \rightarrow \text{MnO}_2 + 2\text{NO}_2$.

Exercises

1. Which is reduced more readily, dilute HNO_3 or dilute HNO_2 ? Which then is the better oxidizing agent?
2. Can you explain why the oxidation potential of HNO_3 is so much reduced by dilution?
3. Besides Mn^{++} , cite a substance oxidized by $\text{PbO}_2 + \text{H}^+$, but not by HNO_3 alone.
4. Is the KNO_3 in black gunpowder an oxidizing agent at ordinary temperatures?
5. Outline a brief method for testing for NO_3^- and ClO_3^- in the presence of each other.
6. How would you test for ClO_3^- in the presence of Cl^- ?
7. Complete and balance the following equation: $\text{NO}_3^- + ? \rightarrow \text{NH}_3 + ?$
8. How would you test for ClO_4^- upon a material containing ClO_3^- ?
9. Assuming that the solubility of KClO_3 is 0.5 mole per liter, calculate its solubility product on the basis of 95 per cent ionization. Calculate its solubility in (a) M KCl (90 per cent ionized) and (b) $0.1 M$ $\text{Ba}(\text{ClO}_3)_2$ (80 per cent ionized).
10. Write equations for the reduction of acidified solutions of ClO_3^- by the following: Sn^{++} , H_2SO_3 , HI , Al , As_2S_3 .
11. Devise a procedure for testing a mixture for Cl^- , ClO_3^- , and ClO_4^- .

12. Why is it dangerous to prepare Cl_2 by the action of concentrated HCl on KClO_3 ?

13. What are the possible anions in a permanganate solution containing Ag^+ and H^+ ?

14. What is the ratio of the oxidizing efficiencies of KMnO_4 in alkaline and in acid solution?

15. For the same weight, which has the greater oxidizing power, KMnO_4 or MnO_2 ?

16. Excess KMnO_4 in the presence of dilute H_2SO_4 oxidizes H_2S to H_2O and SO_4^{--} . Write the equation.

17. Name five ions (cations and anions) whose presence in acid solution would make the presence of MnO_4^- impossible.

18. Why are NO_2^- and $\text{C}_2\text{H}_3\text{O}_2^-$ considered members of both Groups II and IV?

19. How would you determine as directly as possible whether a given potassium salt were (a) KClO_3 or KClO_4 , (b) KNO_3 or $\text{KC}_2\text{H}_3\text{O}_2$, (c) KNO_3 or KClO_3 ?

20. What weight of urea, $(\text{NH}_2)_2\text{CO}$, would be required to remove the NO_2^- from 85 g. of KNO_3 containing 10 per cent KNO_2 ?

21. A mixture of 3 cc. of 0.4 M KNO_3 and 2 cc. of 0.5 M $\text{Ca}(\text{NO}_3)_2$ is boiled with an excess of zinc dust and concentrated NaOH , distilling the NH_3 liberated into 10 cc. of M HCl . What will be the composition of the resulting solution?

22. Ten cubic centimeters of 0.1 M KMnO_4 is added to an acidified solution containing 0.13 g. of NaHSO_3 . How much 0.2 M $\text{H}_2\text{C}_2\text{O}_4$ will be required to decolorize the solution?

23. What weight of zinc would be required (theoretically) to reduce a mixture of 0.490 g. of KClO_3 to KCl and 0.5055 g. of KNO_3 to NH_3 ?

24. What volume of 0.2 M Ag_2SO_4 should be added to a solution containing 2 cc. each of M KI , M K_2CrO_4 and M KNO_3 , so as to remove the interfering substances in the brown-ring test for NO_3^- ?

25. What weights of KNO_3 , H_2SO_4 , and FeSO_4 would be involved in the preparation of 7 l. of NO (measured under standard conditions)?

26. What volume of 0.4 M $\text{Ba}(\text{NO}_3)_2$ is needed to react completely with a solution containing 3 cc. of M $(\text{NH}_4)_2\text{SO}_4$, 2 cc. of 0.5 M NaF , and 4 cc. of 0.3 M Na_2CO_3 ?

CHAPTER XXIV

ANION GROUP V

This group contains the anions whose Ag^+ salts are soluble in water but whose Ba^{++} salts are insoluble in water and in dilute HNO_3 . The membership is as follows:

Sulfate, SO_4^{--} Fluosilicate, SiF_6^{--}
Fluoride, F^-

SULFATE

In addition to the normal sulfate anion SO_4^{--} , there are probably two other anions of hexavalent sulfur, *viz.*: hydrogen sulfate, HSO_4^- ; and pyrosulfate, $\text{S}_2\text{O}_7^{--}$. Upon dilution, these rapidly form SO_4^{--} ions and therefore give all the reactions of SO_4^{--} . So SO_4^{--} only will be considered.

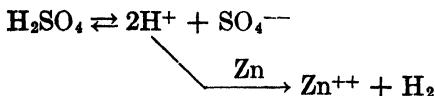
The Acid.—Sulfuric acid, H_2SO_4 , is a colorless oily liquid, having a density of 1.838 and boiling at 270° with slight decomposition (loss of SO_3). A 98.3 per cent mixture boils at 338° without change in composition. The concentrated H_2SO_4 of commerce contains about 95 per cent H_2SO_4 , and the dilute H_2SO_4 of the laboratory contains about 25 per cent H_2SO_4 and is about 3 molar. "Fuming H_2SO_4 " is formed by adding SO_3 to concentrated H_2SO_4 and is assumed to contain pyrosulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$.

Sulfuric acid is prepared by combining SO_2 with the oxygen of the air under the influence of a catalyst and dissolving the resultant SO_3 in water.

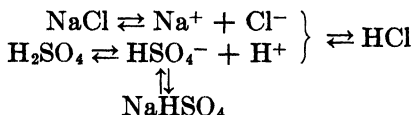
The properties of H_2SO_4 can be grouped under three heads.

Acidic Properties.—Sulfuric acid is a strong acid, though hardly so strong as HCl and HNO_3 . Its ionization approaches 100 per cent upon high dilution; on the other hand, with increasing concentration, the molar conductance diminishes, so that concentrated H_2SO_4 is considered a weak acid.

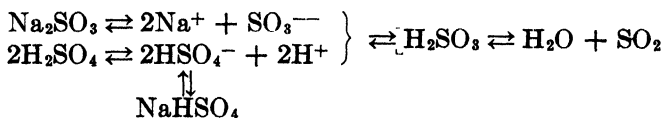
By reason of its ionization, dilute H_2SO_4 reacts with the active metals, liberating H_2 ; *e.g.*,



Another group of reactions of H_2SO_4 follows from a combination of its ionization and its high boiling point. To illustrate: If a salt of a volatile acid is heated with concentrated H_2SO_4 , the volatile acid, or its decomposition products, will be "displaced." For example,

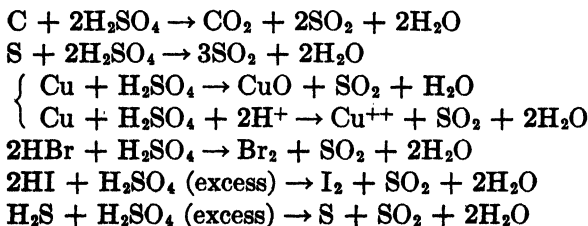


This follows from the fact that, of the four molecular species that may be assumed to be present, HCl is the one with the lowest boiling point and is therefore the one displaced. The expulsion of CO_2 from carbonates or of SO_2 from sulfites may be explained similarly. For example,

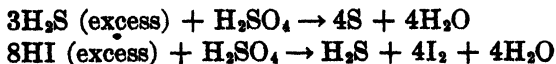


Oxidizing Properties.—Concentrated H_2SO_4 , especially upon warming, is an oxidizing agent of moderate strength. This action seems to be connected with its tendency to decompose upon heating: $\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2$.

With most reducing agents, H_2SO_4 is reduced to SO_2 ; *e.g.*,

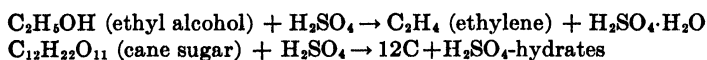


Very active reducing agents, on the other hand, may reduce H_2SO_4 to S , or even to H_2S ; *e.g.*,



Dehydrating Action.—Concentrated H_2SO_4 combines with water vigorously, with the liberation of considerable heat, forming stable hydrates (*e.g.*, $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$). For this reason, it is frequently used as a drying agent for materials with which it does not react.

Concentrated H_2SO_4 not only takes up free water but also will extract hydrogen and oxygen from certain substances in the ratio $2\text{H}:\text{O}$. For example,



The separation of free carbon as a residue is known as *charring* (*cf.* the preceding equation). Frequently charring is accompanied by oxidation-reduction effects. The carbon may be oxidized to CO or CO_2 and the H_2SO_4 reduced to SO_2 . An example of this process is the reaction of H_2SO_4 with tartrates (page 367).

Solubilities.—All sulfates are soluble in water with the following exceptions: PbSO_4 , BaSO_4 , SrSO_4 . CaSO_4 is slightly soluble. Some of the soluble sulfates are hydrolyzed upon boiling, forming basic sulfates that are insoluble; *e.g.*, $\text{Fe}(\text{OH})\text{SO}_4$.

Reactions.—The SO_4^{--} ion has only a few reactions that are of analytical importance.

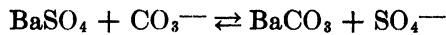
Barium Sulfate.—The Ba^{++} ion precipitates SO_4^{--} as white BaSO_4 . The solubility of this salt in water is very low—only about 0.00001 mole per liter. As a result of this low solubility in water, its solubility in even strong electrolytes (*e.g.*, HCl) is practically negligible.

Strontium Sulfate.—This salt is similar to BaSO_4 in its formation and properties, but somewhat more soluble (about 0.0004 mole per liter). In the presence of alcohol, its solubility is much less, and its precipitation is considered analytically complete.

Calcium Sulfate.—This sulfate is analogous to the other alkaline earth sulfates but is decidedly more soluble (about 0.015 mole per liter). Alcohol reduces its solubility.

Lead Sulfate.—This salt has been described on page 192. Its solubility in water is about 0.0001 mole per liter, and the presence of an excess of Pb^{++} or SO_4^{--} ions is necessary for its complete precipitation. The precipitate may be washed with alcohol without appreciable loss.

Transposition of Barium Sulfate by Sodium Carbonate.— BaSO_4 that has not been ignited may be brought into solution by digesting with a considerable excess of Na_2CO_3 solution, and, after filtering, dissolving the BaCO_3 in HCl or HNO_3 . The reaction may be represented:



In this solution, which is saturated with both BaSO_4 and BaCO_3 , the solubility products of both must be realized.

$$[\text{Ba}^{++}][\text{SO}_4^{--}] = 1.2 \times 10^{-10}$$

$$[\text{Ba}^{++}][\text{CO}_3^{--}] = 6 \times 10^{-9}$$

Since there can be only one value for the concentration of Ba^{++} ions in a single solution, this factor may be eliminated by dividing these expressions.

$$\frac{[\text{Ba}^{++}][\text{SO}_4^{--}]}{[\text{Ba}^{++}][\text{CO}_3^{--}]} = \frac{1.2 \times 10^{-10}}{6 \times 10^{-9}}$$

Simplifying,

$$\frac{[\text{SO}_4^{--}]}{[\text{CO}_3^{--}]} = \frac{1}{50}$$

That is, the concentration of the CO_3^{--} ion must be fifty times that of the SO_4^{--} .

Suppose that 1 mole of BaSO_4 is present and Na_2CO_3 is added until the final CO_3^{--} concentration is 50 molar. The concentration of the SO_4^{--} ion must then be 1 molar, which calls for the complete solution of the BaSO_4 . Since 1 mole of BaCO_3 is precipitated and 50 moles of CO_3^{--} remain in solution (assuming complete ionization), the total Na_2CO_3 added must be $1 + 50$, or 51. Since equilibrium is never realized except by prolonging boiling, the amount of Na_2CO_3 required is always in excess of this theoretical amount.

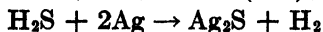
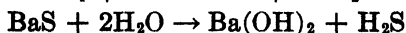
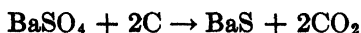
If the BaSO_4 is in the form of the mineral barite, or if it has been ignited, it is better to powder it and fuse it with solid Na_2CO_3 . After cooling, the melt is extracted with hot water, the soluble Na_2SO_4 being thus removed and the insoluble BaCO_3 left in the residue.

In either case, more than one treatment may be necessary to convert BaSO_4 completely into BaCO_3 .

Detection.—The SO_4^{--} ion is usually detected by its formation with Ba^{++} ions of a precipitate of BaSO_4 , insoluble in dilute HNO_3 or dilute HCl . In this book, $\text{Ba}(\text{NO}_3)_2$ is used as a precipitant instead of BaCl_2 ; for the Cl^- of the latter is apt to interfere by throwing down precipitates of insoluble chlorides, such as AgCl or Hg_2Cl_2 . A precaution to be observed in the use of $\text{Ba}(\text{NO}_3)_2$ is that the solution of this reagent should be, not saturated, but rather fairly dilute. Otherwise, an excess of NO_3^- in the material to be tested may precipitate $\text{Ba}(\text{NO}_3)_2$, which might be mistaken for BaSO_4 . This precipitation seems to be due to a combination of the common-ion and salt effects (see page 194).

Sulfates insoluble in dilute acids may be detected in two ways: (1) The powdered material is boiled with concentrated Na_2CO_3 solution for some time, the sulfate being thus transposed into an insoluble carbonate. After filtering, the SO_4^{--} in the filtrate may be detected in the usual way. (2) The powdered material, when heated to redness in the presence of charcoal in a covered crucible, forms a mixture of sulfite and sulfide. The product is acidified with HCl , and the evolution of SO_2 or H_2S , or the separation of free sulfur, indicates the presence of the sulfate group in the original. Insoluble sulfides interfere with this test. Sulfites and thiosulfates will also interfere, but they are usually easily separated from the insoluble sulfate before heating with charcoal.

The Hepar Test.—A modification of the preceding reaction consists in reducing the sulfate to a sulfide by heating it in the reducing flame on a piece of charcoal in the presence of Na_2CO_3 . The reduction product is then scraped off the charcoal by means of a spatula or knife blade and transferred to a *clean* silver coin. Upon moistening, a brown stain due to Ag_2S develops; *e.g.*,



This reaction is known as the *hepar reaction* and dates back to antiquity. The word *hepar* comes from the Greek and means liver. It seems to have been used because many sulfides show a

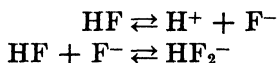
liver-color; *e.g.*, antimony sulfide was once known as the *liver of antimony*.

FLUORIDE

Fluorides have a number of practical uses, which bring them on the market in large quantities.

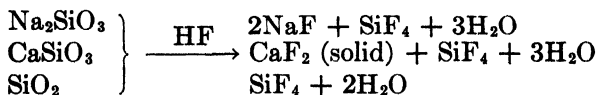
The element fluorine occurs in nature as fluorspar or fluorite, CaF_2 . Besides being the source material for other fluorine compounds, this mineral is used as a flux in metallurgy (*e.g.*, in the preparation of metallic aluminum) and as a constituent of enamels and certain glasses. Sodium fluoride, NaF , is used as an antiseptic in the brewing industry and as a bane for insects, rats, etc.

The Acid.—Hydrogen fluoride is a colorless gas, liquefying at 19.4° . Formerly it was thought to have the composition H_2F_2 , but recent work indicates that this is not the case and that only the ions represented in the following equilibriums are present:



For the sake of simplicity, the formula HF is used in this book.

Hydrogen fluoride is very soluble in water, giving a solution that is weakly acidic. For example, 0.1 *M* HF is only 10 per cent ionized, indicating that it is somewhat stronger than $\text{HC}_2\text{H}_3\text{O}_2$ but not so strong as H_3PO_4 . The acid attacks ("etches") glass, forming SiF_4 , etc. For example, with ordinary soda-lime glass, its action may be diagrammed as follows:



Hydrofluoric acid is prepared industrially by distilling a mixture of CaF_2 and concentrated H_2SO_4 in lead-lined apparatus. The commercial product contains about 50 per cent HF and comes on the market in wax, hard-rubber, or lead containers. It is used in the ceramic industry and as a sterilizing agent in the brewing and baking industries.

Solubilities.—The fluorides of Na^+ , K^+ , NH_4^+ , Ag^+ , Al^{+++} , Sn^{++++} , and Hg^{++} are readily soluble in water. Others are insoluble, or at least only sparingly soluble. The most insoluble are PbF_2 , BaF_2 , SrF_2 , CaF_2 , and CeF_3 .

Reactions.—The principal analytical reactions of the F^- ion are as follows.

Precipitation of Barium Fluoride.— F^- ions are precipitated by Ba^{++} solutions, giving white BaF_2 . This salt has an appreciable solubility in water— 7×10^{-3} mole per liter. In the presence of strong electrolytes, such as the mineral acids and NH_4^+ salts, BaF_2 becomes fairly soluble.

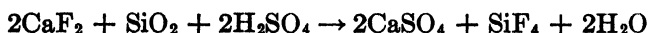
Calcium Fluoride.— F^- ions combine with Ca^{++} , forming white slimy CaF_2 . The solubility of CaF_2 is 2×10^{-4} mole per liter, which is somewhat less than that of BaF_2 . Still it is not low enough to prevent strong electrolytes having an appreciable solvent action. NH_4^+ salts in particular tend to increase the solubility of CaF_2 .

Cerous Fluoride.—Cerous ions Ce^{+++} precipitate F^- ions as white CeF_3 , insoluble in dilute HNO_3 . This is apparently the most insoluble fluoride.

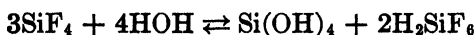
Displacement by Concentrated H_2SO_4 .— HF is displaced when solid fluorides are warmed with concentrated H_2SO_4 ; e.g., $CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$. This reaction is favored by (1) the volatility of HF and (2) its low ionization.

Formation of Silicon Tetrafluoride.— HF tends to react with SiO_2 according to the equation $SiO_2 + 4HF \rightleftharpoons SiF_4 + 2H_2O$. Ordinarily, the equilibrium is far to the left; but, in the presence of an active dehydrating agent, such as concentrated H_2SO_4 , the reaction proceeds to the right.

The formation of SiF_4 from a fluoride can be made to proceed in one operation when a mixture of a fluoride and fine sand is warmed with concentrated H_2SO_4 . An illustrative equation, combining the successive reactions, is the following:



Silicon tetrafluoride is a colorless gas which combines readily with water, forming a precipitate of $Si(OH)_4$.



This reaction is the basis of the drop-of-water test for fluoride. When a drop of water, suspended in a loop of platinum wire or on a glass rod, is brought into SiF_4 vapors, it becomes turbid, owing to the formation of a precipitate of $Si(OH)_4$.

Detection.—The following reactions are used in the detection of F^- : (1) The precipitation of white BaF_2 (or CaF_2), insoluble in dilute HNO_3 . (2) The formation of white CeF_3 , insoluble in strong acids. The following anions interfere by forming precipitates with Ce^{+++} : $C_2O_4^{--}$, PO_4^{--} , AsO_4^{--} , AsO_3^{--} , and $Fe(CN)_6^{--}$. (3) The evolution of SiF_4 when a mixture of fluoride and SiO_2 is warmed with 90 per cent H_2SO_4 . This gas may be detected by its formation of a turbidity with a drop of water.

FLUOSILICATE

Formerly fluosilicic acid and its salts were almost unknown outside of academic laboratories. Now the acid is manufactured in large quantities and used in preparing some important industrial salts. Sodium fluosilicate, Na_2SiF_6 , is used as an insecticide in poultry houses; magnesium fluosilicate, $MgSiF_6$, is used as a dressing to harden concrete floors; and copper fluosilicate, $CuSiF_6$, is used in staining marble surfaces. Fluosilicates have now become so important that the analytical scheme must be modified so as to include the SiF_6^{--} ion.

The Acid.—Fluosilicic acid, H_2SiF_6 (also called *hydrofluosilicic*, *silicofluoric* and *hydrosilicofluoric* acid), is prepared in the laboratory by warming a mixture of CaF_2 , SiO_2 , and H_2SO_4 and absorbing the SiF_4 evolved in water: $3SiF_4 + 4HOH \rightarrow 2H_2SiF_6 + Si(OH)_4$. The $Si(OH)_4$ precipitate is separated by decantation or filtration. Fluosilicic acid is obtained industrially as a by-product in making calcium "superphosphate," $Ca(H_2PO_4)_2$. CaF_2 and SiO_2 are present as impurities in the crude rock phosphate and react with H_2SO_4 as in the laboratory procedure.

The commercial product is a colorless, fuming solution, containing up to 30 per cent H_2SiF_6 . Attempts to concentrate it beyond this point cause decomposition: $H_2SiF_6 \rightarrow 2HF + SiF_4$.

Fluosilicic acid is a moderately strong acid, about 50 per cent ionized in molar solution. Dilute solutions attack glass only slightly, indicating very little tendency to dissociate into HF and SiF_4 . With higher concentrations, there is an increase in the amount of HF and a corresponding increase in the amount of attack.

Solubilities.—Most fluosilicates are soluble in water. The most insoluble fluosilicate is $BaSiF_6$, with a solubility of 0.0015

mole per liter. K_2SiF_6 is considerably more soluble (about 0.005 mole per liter), though this solubility may be largely reduced by adding alcohol.

Reactions.—In view of the few insoluble silicates, there are few reactions of analytical use.

Barium Fluosilicate.— Ba^{++} ions precipitate SiF_6^{--} as white $BaSiF_6$, difficultly soluble in dilute acids.

Potassium Fluosilicate.— K_2SiF_6 is a white, gelatinous precipitate, formed by the union of K^+ and SiF_6^{--} ions. It is slightly soluble in water but quite insoluble in alcohol. Owing to the high ionization of H_2SiF_6 , the solvent action of strong acids on this salt is low.

Decomposition by Bases.—Soluble fluosilicates are decomposed by bases: $SiF_6^{--} + 4OH^- \rightarrow SiO_2 \cdot xH_2O + 6F^-$. This reaction goes to completion by reason of the insolubility of the $SiO_2 \cdot xH_2O$.

Detection.—The detection of the SiF_6^{--} ion is based on the following reactions: (1) the formation with $Ba(NO_3)_2$ of a white precipitate of $BaSiF_6$, insoluble in dilute HNO_3 ; (2) the formation with KCl of white K_2SiF_6 , insoluble in dilute alcoholic solution; (3) the evolution of SiF_4 fumes when a solid fluosilicate is warmed with concentrated H_2SO_4 . The SiF_4 may be detected by the drop-of-water test (page 408). The presence of a mixture of SiO_2 (or a silicate) and a fluoride interferes with this test.

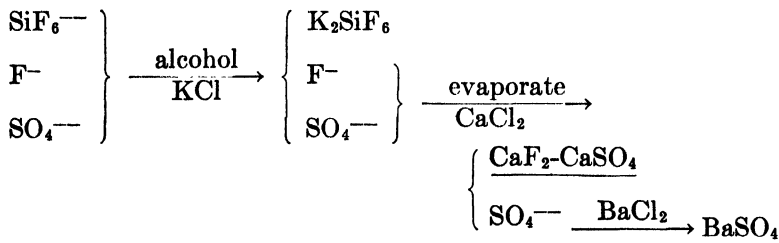
SPECIAL ANALYTICAL PROCEDURES

Nonprecipitation of Barium Fluoride.—Barium fluoride is appreciably soluble in strong acids and in NH_4^+ solution, so that frequently it fails to give a precipitate with the reagent, $Ba(NO_3)_2$. It is well to regard F^- as also being a member of Group IV—*i.e.*, to make a test for F^- on the original, even if its presence is not indicated by the Group V reagent.

Sulfate in the Presence of Sulfite and Thiosulfate.—The insolubility of the Ba^{++} precipitate in HNO_3 is sufficient evidence that the precipitate is not $BaSO_3$. On the other hand, if SO_3^{--} has previously been found, the presence of a small amount of SO_4^{--} may be presumed, since sulfites and, to a less degree, thiosulfates always contain SO_4^{--} as an impurity. Solutions of sulfites appear to oxidize slowly in the air.

Complication in the Sulfate Test by Excess Nitrate.—Barium nitrate is practically insoluble in concentrated NO_3^- solutions, so that a precipitate of $\text{Ba}(\text{NO}_3)_2$ sometimes forms when Ba^{++} is added to solutions of high NO_3^- concentration. This precipitate can be distinguished from BaSO_4 by its solubility in warm water.

Detection of Sulfate, Fluoride, and Fluosilicate in the Presence of One Another.—This unusual combination is met in solutions containing only those cations whose salts with Group V anions are soluble—*e.g.*, Ag^+ , Mg^{++} , etc. The SiF_6^{--} is first precipitated as K_2SiF_6 by means of KCl in a 50 per cent alcoholic solution. After removal of the alcohol by evaporation, CaCl_2 is added, precipitating F^- as CaF_2 and partially precipitating SO_4^{--} as CaSO_4 . The filtrate, which may be considered a saturated solution of CaSO_4 , is next tested for SO_4^{--} by BaCl_2 . This procedure may be outlined thus:



These precipitates should be confirmed by appropriate tests.

The alcohol must be removed by evaporation, since its presence might bring about the complete precipitation of CaSO_4 .

Exercises

1. Outline a procedure for converting BaSO_4 quantitatively into *c. p.* BaCl_2 .
2. Starting with NaF , how would you prepare pure KF ?
3. Refer to the Solubility Table, and see if you can devise another method for separating SO_4^{--} from F^- .
4. How would you distinguish K_2SO_4 from KHSO_4 and $\text{K}_2\text{S}_2\text{O}_7$?
5. Nitrates may be converted into chlorides by evaporating with an excess of HCl . Is this action analogous to the displacement of HCl by concentrated H_2SO_4 ?
6. Why does dilute H_2SO_4 fail to react with carbon, sulfur, etc.?
7. Suppose that 1 mole of SO_3 is introduced into a solution molar in Ba^{++} and molar in Sr^{++} . Prove that BaSO_4 and SrSO_4 would be precipitated in the ratio 1,600:1.

8. One mole of BaCl_2 is added to a solution containing 1 gram ion each of CO_3^{--} and SO_4^{--} . How much of each will be precipitated?

9. Is the reduction of the solubility of CaSO_4 by alcohol due to a diminution of the concentration of CaSO_4 molecules or of its ions?

10. How would you test for SO_4^{--} in a solution containing SO_3^{--} and $\text{S}_2\text{O}_3^{--}$?

11. Outline a procedure for the detection of the anions in the mixture $\text{BaSO}_4 + \text{BaF}_2 + \text{BaSiF}_6$.

12. How would you test for HF in the presence of H_2SiF_6 ?

13. How would you test Na_2SiF_6 for NaF?

14. A mixture of Group V anions gave the following reactions: a white precipitate with $\text{Ba}(\text{NO}_3)_2$, but none with $\text{Ca}(\text{NO}_3)_2$; with NH_4OH a gelatinous white precipitate, and a filtrate which, after evaporation to a residue, gave with $\text{SiO}_2 +$ concentrated H_2SO_4 a gas that formed a turbidity with a drop of water. What ions are indicated?

CHAPTER XXV

ANION GROUP VI

This group contains the anions that, upon acidification and evaporation, leave an insoluble residue of SiO_2 . It consists of the various silicate ions.

The Element Silicon.—Certain metals and alloys contain silicon as silicides. When they are dissolved in nonoxidizing acids, most of the silicon is evolved as gaseous silicon hydride, SiH_4 , though some may separate in the free form as a dark brown powder. If the metal or alloy is dissolved in HNO_3 or aqua regia, the silicon is left as white $\text{SiO}_2 \cdot x\text{H}_2\text{O}$, which may be detected as such (see following paragraphs).

SILICATES

Several types of silicates are found in nature, corresponding to the following anions:

SiO_4^{--} , orthosilicate
 SiO_3^{--} , metasilicate

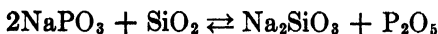
$\text{Si}_2\text{O}_7^{--}$, disilicate
 $\text{Si}_3\text{O}_8^{--}$, trisilicate, etc.

Silicic Acids.—The existence in the free state of acids corresponding to the above anions is problematical. When a soluble silicate is acidified, hydrated silica, $\text{SiO}_2 \cdot x\text{H}_2\text{O}$, is thrown down as an amorphous, gelatinous mass; *e.g.*,



The precipitate thus obtained is frequently called *silicic acid*, though it is better to regard it as a hydrated oxide. It is appreciably soluble in water and acids, is readily soluble in strong alkalis (*e.g.*, NaOH), and fairly soluble in Na_2CO_3 . Upon slow evaporation at room temperature or upon gentle heating, it gradually loses water, and leaves residues of increasing insolubility. Silicic acid, dried by heating the hydrated silica at 120° for 1 hr., becomes practically insoluble in acids but still may be dissolved by heating in alkaline solutions.

An analogous reaction does not occur when SiO_2 is heated with a NaPO_3 bead, owing to the nonvolatility of P_2O_5 .



Most of the SiO_2 remains undissolved, and hence the NaPO_3 - SiO_2 bead is opaque.

Detection.—Since silicates are generally broken down and separated as $\text{SiO}_2 \cdot x\text{H}_2\text{O}$, their detection consists in testing for SiO_2 . The following reactions are used: (1) Gaseous SiF_4 is formed when the solid material is mixed with powdered CaF_2 and heated with 90 per cent H_2SO_4 . This gas is detected by the drop-of-water test (see page 408). (2) SiO_2 is soluble in beads of fused Na_2CO_3 but not in beads of fused NaPO_3 . In the latter case, the opaque mass is called a *silica skeleton*.

Exercises

1. Name some solutions besides alkaline silicates that form precipitates upon acidification.
2. How would you distinguish between Na_2SiF_6 and a mixture of Na_2SiO_3 and NaF ?
3. In fusions of silicates with Na_2CO_3 , what metals are converted into carbonates, and what metals into oxides?
4. If Al_2O_3 , Fe_2O_3 , etc., do not form carbonates in fusions with Na_2CO_3 , how do you explain their change into a soluble form?
5. Predict the reaction when SiO_2 is heated with (a) NaNO_3 , (b) NaCl , (c) Na_2SO_3 , (d) Na_3AsO_4 . Explain your answer.
6. What volume of 25 *M* HF is involved in dissolving a mixture of 0.180 g. of SiO_2 and 0.416 g. of MgSiF_6 in the presence of concentrated H_2SO_4 ?
7. Outline a procedure for the analysis of ordinary soda-lime glass, Na_2SiO_3 - CaSiO_3 - SiO_2 .
8. Suppose 5.4 g. of pure SiO_2 is dissolved in excess HF and the SiF_4 formed is dissolved in 200 cc. of water. Calculate the concentration of the H_2SiF_6 formed.
9. Is a large excess of Na_2CO_3 necessary in converting SiO_2 into Na_2SiO_3 by fusion? Compare the transposition of BaSO_4 by Na_2CO_3 , and explain the difference.
10. Why is fused borax inferior to fused Na_2CO_3 as a solvent for SiO_2 ?

CHAPTER XXVI

DRY REACTIONS OF ANALYTICAL CHEMISTRY

Most of the reactions of analytical chemistry are "wet" reactions; *i.e.*, they proceed in the presence of liquids which serve as reaction mediums. There remain to be considered certain types of reaction that occur at high temperatures and in the absence of ordinary solvents and that are known as "dry" reactions.

BLOWPIPE ANALYSIS

Fifty years ago, the general procedure for the detection of the metals in an unknown substance was to subject it to a small-scale smelting operation. A powdered sample of the unknown was heated on a piece of charcoal, a blowpipe being used to provide the blast, oxidizing or reducing as required. Fluxes were added to float out inert materials.

Strictly speaking, blowpipe analysis is of prehistoric origin. It may be imagined that it had its beginning in an event such as this: One of our early ancestors, more observant than the rest, noticed that there sometimes occurred in the ashes of his campfire heavy, more or less metallic clinkers, which he could hammer into spearheads, or even knives. In some way he associated these new substances either with the wood that he burned or with the stones of which he built his hearth. Further observation showed that the stones were responsible, and still further observation showed that only certain kinds of stones gave the new substances. This led him to try various kinds of stones, in order to find out which of them gave the best yields. In the course of time, he came to carry out the operation, not primarily for the warmth afforded, but for the sake of the clinkers. Before making a large-scale run, he learned to try out small samples to be sure of obtaining a supply of the desired product.

Although many of the steps of fire analysis are very old, major credit for blowpipe analysis goes to the Swedish chemist Berzelius, who about 1820 put the procedures on a practical, systematic

basis. While superseded in chemical laboratories by wet processes, blowpipe analysis is still used by prospectors in field work and in mineralogical laboratories. It has the advantage of requiring very simple apparatus—a spirit lamp, a brass blowpipe, a few bottles of dry chemicals, and a few solutions.

The general procedure consists in heating the powdered material in a cavity in a piece of charcoal and adding certain fluxes to remove worthless materials. Both oxidizing and reducing flames are employed (Fig. 31). The oxidizing flame is produced by placing the tip of the blowpipe in the outer envelope of the Bunsen flame and projecting the flame on the charcoal. In this way, an excess of oxygen is present, giving oxidizing action at a high temperature. The reducing flame is obtained by projecting

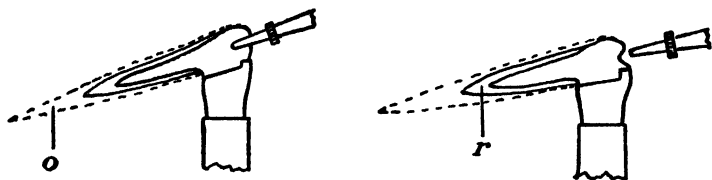


FIG. 31.—Oxidizing and reducing blowpipe flames.

the inner, or luminous, flame on the material on the charcoal. The temperature obtained is not so high, and the excess of gas present provides a reducing atmosphere. It should be pointed out that easily reduced oxides are reduced under the oxidizing flame. This is largely due to CO formed by the action of the excess carbon. The presence of a metal is indicated by the formation of sublimates, coatings or incrustations, or globules characteristic of the element. The oxides of the baser metals are not reduced but combine with the flux, forming a slag which tends to be absorbed by the charcoal. The results are confirmed by other tests, such as the heating of coatings with $\text{Co}(\text{NO}_3)_2$ and the malleability and solubility of metals in HNO_3 .

The principal reactions of blowpipe analysis are indicated in Table 41.

BEAD TESTS

Certain fused salts—particularly Na_2CO_3 , $\text{Na}_2\text{B}_4\text{O}_7$, and NaPO_3 —have the property of dissolving oxides, depending on their nature. Sometimes colors or other distinctive reactions

are obtained that may be used in the identification of various elements. These beads are made by making a loop in a platinum wire, heating it to redness, bringing it into contact with a small

TABLE 41.—THE REACTIONS OF BLOWPIPE ANALYSIS

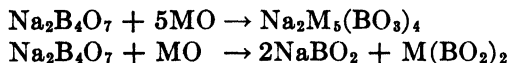
Reaction upon Heating with Oxidizing Flame on Charcoal	Element Indicated
Volatilization, leaving no residue:	
Purple flame.....	Sulfur
No fumes, sometimes forming precipitate...	Ammonium
White fumes, white coating.....	Mercury salts
White fumes, garlic odor.....	Arsenic
Fusion, giving a clear melt, but no fumes or coating:	
Flame test: Yellow.....	Sodium
Purple.....	Potassium
White residue, nonvolatile, alkaline to litmus:	
Flame test: Orange-red.....	Calcium
Crimson.....	Strontium
Green.....	Barium
None.....	Magnesium
White residue, nonvolatile, neutral to litmus, giving upon ignition with $\text{Co}(\text{NO}_3)_2$:	
A blue mass.....	Aluminum
A green mass.....	Zinc
Colored residue, white fumes, leaving a residue that is	
White when hot, yellow when cold.....	Zinc
Yellow-brown, very volatile.....	Cadmium
Colored residue, no coating. The borax bead test is	
Blue (hot), blue (cold).....	Cobalt
Green (hot), blue (cold).....	Copper
Green (hot), green (cold).....	Chromium
Purple (hot), violet (cold).....	Manganese
Red-brown (hot), violet (cold).....	Nickel
Orange (hot), yellow (cold).....	Iron
Metallic bead or scales:	
Red, hard, malleable.....	Copper
White, malleable, soft; yellow coating.....	Lead
White, brittle; yellow coating.....	Tin
White, brittle; white coating.....	Antimony
White, brittle; yellow coating.....	Bismuth

amount of flux, and heating until a clear drop is formed. If the bead is too small, more of the flux may be added. The hot bead is then brought into contact with a minute amount of the sub-

stance to be tested and reheated until the reaction is complete. After standing, these beads become opaque, probably owing to devitrification.

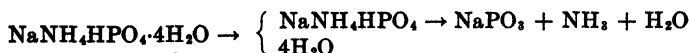
Sodium Carbonate Fusions.—Sodium carbonate acts like a base, combining with acidic oxides. This is due to the easy displaceability of CO_2 ; *e.g.*, $\text{Na}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{CO}_2$. This reaction depends on (1) the weakness of carbonic acid, H_2CO_3 , and (2) the volatility of CO_2 . Basic oxides do not dissolve in Na_2CO_3 but are simply suspended in the melt and therefore give opaque beads.

Borax Beads.—When borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, is heated, it loses its water of hydration and leaves a clear melt of sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7$. Upon cooling, this sets, forming a glass which, it will be remembered, is not a true solid but a liquid of very high viscosity. This substance is potentially an acid salt ($\text{Na}_2\text{B}_4\text{O}_7 = 2\text{NaBO}_2 + \text{B}_2\text{O}_3$) and combines with metallic oxides forming beads of unknown composition. Using M as the symbol for a divalent metal, hypothetical equations like the following have been suggested:



The borax bead will not dissolve acidic oxides unless the corresponding acids are very reactive— P_2O_5 and SO_3 , for example. B_2O_3 is not volatile enough to be displaced by the anhydrides of weak acids. For example, SiO_2 does not dissolve in $\text{Na}_2\text{B}_4\text{O}_7$ but gives an opaque suspension (silica skeleton).

Metaphosphate Beads.—When heated, sodium ammonium hydrogen phosphate, $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$, decomposes, leaving a melt of sodium metaphosphate.



Sodium metaphosphate combines with metallic oxides, forming compounds of undetermined composition, presumably orthophosphates. A possible equation is: $\text{NaPO}_3 + \text{MO} \rightarrow \text{NaMPO}_4$. Owing to the low volatility and weak acidity of P_2O_5 , NaPO_3 does not react with weakly acidic oxides, such as SiO_2 , CO_2 , etc.

Interferences.—A large number of materials are not transposed by these beads but form opaque suspensions that vitiate other

tests. CaF_2 , for example, makes the bead opaque and white, covering up color reactions so that they are of doubtful significance. Bead tests, therefore, should be carried out only on materials that have been separated in the pure state and not on mixtures.

Oxidizing and Reducing Effects.—The outer zone of the Bunsen flame has been seen to be an oxidizing region (page 417),

TABLE 42.—BEAD REACTIONS

Element	Borax bead		Metaphosphate bead	
	Oxidizing flame	Reducing flame	Oxidizing flame	Reducing flame
Cu.....	{ Blue (cold) Green (hot)	Red	{ Blue (cold) Green (hot)	Red (cold)
Fe.....	Yellow-brown-red	Green	Yellow-brown	Green
Cr.....	{ Green (cold) Yellow (hot)	Green	Green	Green
Mn.....	Amethyst	Colorless	Amethyst	Colorless
Co.....	Blue	Blue	Blue	Blue
Ni.....	{ Brown (cold) Reddish (hot)	Opaque	{ Brown (cold) Reddish (hot)	Opaque
Si(SiO_2).....	Opaque	Opaque	Opaque	Opaque
Fe + Co.....	Green	Green
Ag, Pb, Sb, Cd, Bi, Zn, Ni.....	Opaque	Opaque

and therefore metallic oxides heated in it are generally oxidized to their highest valences. The inner zone, on the contrary, is a reducing region, and reducible oxides are changed to lower valences or even to the free metal. In the oxidizing flame, Fe^{++} is oxidized to Fe^{+++} (brown); Mn^{++} is incompletely oxidized to a mixture of MnO_2 (black) and MnO_4^- (purple), giving amethyst as the resultant color; Cr^{+++} cannot be oxidized to CrO_4^- except in alkaline medium and consequently remains green in the borax and metaphosphate beads. In the reducing flame, Cu^{++} is reduced to Cu_2O (red), MnO_2 to Mn^{++} (colorless), Fe^{+++} to Fe^{++} (colorless to green), and zinc and most of the metals below it in the e.m.f. series are reduced to the metallic form and give opaque, gray beads.

Ignition Reactions.—Many solid substances, when heated in dry test tubes, show reactions that are more or less distinctive (see Table 43).

TABLE 43.—IGNITION REACTIONS

Reaction	Substances Indicated
I. A gas is evolved, which is	
Colorless, condensing to water.....	Water of hydration
Colorless, giving odor of H_2S	Hydrated sulfides and sulfites
Colorless, giving odor of SO_2	Certain sulfites and thiosulfates
Colorless, consisting of O_2	Chlorates, peroxides
Yellowish, consisting of NO , NO_2	Nitrate, nitrite
II. A sublimate is formed, which is	
White, soluble in water.....	$HgCl_2$, NH_4Cl , $H_2C_2O_4$
White, blackened by NH_3	Hg_2Cl_2
White, soluble in $NaOH$	As_2O_3
Yellow, soluble in CS_2	S
Reddish-yellow (stain).....	$FeCl_3$
Blue-black (violet vapor).....	I
Gray film, forming bright drops upon rubbing	Hg
Steel-gray ("mirror").....	As
III. The substance changes color	
Charring, with odor of burnt sugar.....	Organic material
White (cold) \rightleftharpoons yellow (hot).....	ZnO
White (cold) \rightarrow orange (hot) \rightarrow yellow (cold)	Bi_2O_3
Yellow (cold) \rightarrow yellow (hot).....	PbO
Yellow (cold) \rightleftharpoons brown (hot).....	SnO_2
Blackening, but with no odor of burnt sugar.	Cu and Co compounds

FLAME TESTS, SPECTRUM ANALYSIS

Upon strong heating, many salts form gases that emit characteristic flame colors. With the exception of sodium salts, which give a pure yellow light, the flame colors are mixtures of two or more simple colors (see Table 44).

Flame colors are generally characteristic of the metallic element and independent of the nature of the acid radical.¹ Most physicists interpret this to mean that salts are dissociated in the flame into ions, and the gaseous ions are responsible for the

¹ An exception is found in cupric salts, which show different flame colors. $CuCl_2$ gives a green color, and $Cu(NO_3)_2$ a blue. This difference is probably due to the complexity of $CuCl_2$.

colors. This view is supported by the fact that salt vapors are conductors of electricity.

As just stated, volatility is prerequisite to the formation of colored vapors. Most of the salts of the alkali and alkaline earth metals (not including magnesium) and copper are volatile enough to color the Bunsen flame (1500 to 1600°). In order to volatilize the salts of other metals, the electric arc or spark (about 3700°) is used.

TABLE 44.—FLAME COLORS

Element	Color
Na ⁺	Yellow
K ⁺	Purple (red + deep blue)
Ca ⁺⁺	Peach red (red + yellow)
Sr ⁺⁺	Deep red (red + blue)
Li ⁺	Crimson (red + orange)
Ba ⁺⁺	Green (containing weak red and yellow)
Cu ⁺⁺	Green to blue
H ₃ BO ₃	Green

The kind of light emitted by glowing gases therefore gives a means of identifying the cations. These tests are of two kinds:

(1) flame tests and (2) spectrum analysis.

Flame Tests.—These tests are usually made by introducing small amounts of the solution (sometimes a solid) into the outer shell of the colorless Bunsen flame by means of a platinum wire.



FIG. 32.—
Container for
platinum
wire.

The wire should be previously cleaned by alternately dipping it in concentrated HCl and heating until it gives no color to the flame, or at least only a momentary one. The platinum wire used in flame tests is usually sealed in a piece of glass tubing or rod. It may be protected from rough usage and kept clean in the laboratory locker if it is kept in a test tube containing HCl, the glass handle being fitted into a stopper (Fig. 32). The end of the wire may be bent into a small loop, the better to hold a drop of the liquid or a particle of the solid. The unknown is introduced into the outer zone of the colorless flame, about even with the top of the inner green cone. This portion of the flame is an oxidizing region, owing to the presence of an excess of air from the outside. Except in special cases, the unknown is not heated in the inner cone, since this is a reducing region by reason of an excess of gas (reducing agent). In the reducing flame, the salts of certain cations—particularly Ag⁺, Sn⁺⁺ and Sn⁺⁺⁺⁺, Pb⁺⁺, Cd⁺⁺, and Sb⁺⁺⁺—are reduced to metals which combine readily with platinum, forming alloys of low melting

points. The result is that the wire "melts in two" and is ruined. The flame coloration is best seen when observed edgewise.

Flame tests are best made on concentrated solutions. Furthermore, chlorides, as a rule, give stronger tests than other anions. Hence solutions are evaporated almost to dryness and a few drops of HCl solution added. Excess of HNO_3 should be expelled, for this combines with HCl, forming aqua regia, which attacks platinum. Only the end of the wire is dipped in the solution, because it is difficult to clean the wire near the glass holder.

While the anions give no colors themselves, they are important in influencing volatility. For example, CaCl_2 gives an intense yellow-red flame, CaSO_4 a faint yellow, and CaSiO_3 almost no color at all. CaO is so nonvolatile that it can be heated to white heat without forming any Ca^{++} vapor. (Recall the limelight of early theatrical days.) The addition of HCl transposes many nonvolatile salts more or less, forming chlorides and increasing the sensitiveness of the test.

Sometimes a salt is heated in the reducing flame to convert it into a compound more readily transposed by HCl. CaSO_4 , as just stated, gives a weak flame test. When HCl is added, a certain amount of CaCl_2 is formed, according to the equation $\text{CaSO}_4 + 2\text{HCl} \rightleftharpoons \text{CaCl}_2 + \text{H}_2\text{SO}_4$. But, upon heating, this equilibrium is instantly shifted to the left, owing to the loss of HCl, which is the most volatile component in the equilibrium. Consequently the HCl treatment is ineffective. But if the CaSO_4 is previously heated in the inner flame, it is reduced to CaSO_3 or CaS , and these are irreversibly transposed by HCl, forming CaCl_2 and SO_2 or H_2S .

Interferences.—Flame tests on mixtures are seldom satisfactory. For example, Na compounds, by their great volatility, give an intense yellow color that covers up the colors of other elements. A small amount of Sr or Li plus Na might be mistaken for a test for Ca. Weaker colors, like the green of Ba, may be completely masked by the red of Sr or the purple of K. In such cases, an analysis of the light is desirable. A number of substances have been suggested to filter out interfering colors. Cobalt glass is frequently used to absorb the yellow of the Na flame, so that the purple of the K flame may be visible (see page 311).

Flaming Tests.—A variation of the ordinary flame test is obtained when a test tube containing cold water is dipped in the solution to be tested and then heated in a Bunsen flame. The flame around the tube shows the color characteristic of the cation, and frequently a residue is formed on the outside of the tube (see Table 45). This form of flame reaction is known as a *flaming test*. It is not so sensitive as the platinum-wire method and is subject to a number of interferences.

TABLE 45.—FLAMING TESTS

Ion	Solvent	Flame colors	Residue
Pb ⁺⁺	HNO ₃	Red and yellow-blue	White film
Ag ⁺	HNO ₃	Light-gray film
Cu ⁺⁺	HCl	Blue	Green film
Cu ⁺⁺	HNO ₃	Green	Green film
Bi ⁺⁺⁺	HCl	Steel gray-green in upper edge of flame	Gray-black film
Sn ⁺⁺⁺⁺	HCl	Sky blue	White mistlike film
Sn ⁺⁺	HCl	Better results than with Sn ⁺⁺⁺⁺	White mistlike film
Ni ⁺⁺	HCl	Green	Green film
Al ⁺⁺⁺	HCl	Red	White powder
Cr ⁺⁺⁺	HCl	Yellow-red (volcano-like)	"Lumpy and bubbled", purple color
Zn ⁺⁺	HCl	None	White powder
Ba ⁺⁺	HCl	Gray-green	White film
Sr ⁺⁺	HCl	Red	White film
Ca ⁺⁺	HCl	Yellow-red	White film
K ⁺	HCl	Violet	White powder
Na ⁺	HCl	Yellow	White powder

Spectrum Analysis.—The only safe way to use flame tests as an independent method of analysis is to resolve the light into its component tints and to identify the cations present by their characteristic sets of tints.

Spectra.—When a beam of light from an incandescent solid or liquid is passed through a prism or a diffraction grating, it is broken down into a ribbon of colors, ranging from red to violet. This band of colors is known as a *continuous spectrum* and appears to contain all the different wave lengths of light. On the other hand, if light from an incandescent vapor is passed through a prism, a *bright line* or *emission spectrum* is obtained, according to the tints present in the flame. If sunlight is analyzed in this way, the spectrum is crossed with numerous black lines, called

Fraunhofer lines, after the physicist who first studied them. This is known as a *dark-line spectrum* and is formed by passing a continuous spectrum from an incandescent solid through a layer of incandescent gas. Absorption results, so that each bright line in the emission spectrum has a counterpart in a dark line in the absorption spectrum. By identification of these Fraunhofer lines, the composition of the sun has been approximately determined. Colored solutions give still another type of absorption spectrum—the *band spectrum*. This type of spectrum consists

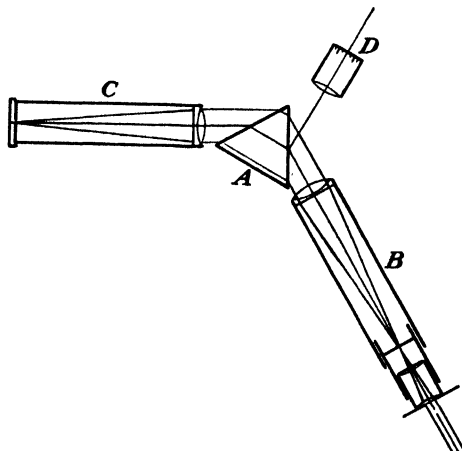


FIG. 33.—The spectroscope.

of groups of bright lines crowded together in places, forming “heads,” the nature and position of which are characteristic of the composition of the solution. Band spectra are due, not to elemental ions, but to larger aggregates of atoms (molecules and complex ions), and are used in the study of solutions, as dyes, drugs, and physiological solutions (blood, for example). Gases in the molecular form also give band spectra.

The Spectroscope.—The instrument used to resolve light into its component colors is called the *spectroscope* and was invented by Bunsen and Kirchhoff in 1860. In its simplest form (Fig. 33), it consists of a prism *A*, mounted on a turntable; the collimator *B*, which throws a beam of parallel rays on the prism; the telescope *C*, through which the spectrum is observed; and the tube *D*, which contains a scale of reference lines which may be superposed upon

the spectrum. The spectroscope is calibrated by observing the spectra of known substances, such as NaCl, KCl, TiCl, etc. These conspicuous lines having been located on the reference scale, the position of other lines in the spectra of unknown substances may be read off and the identity of the component elements determined. Photographic methods are now very important, for they are more sensitive and give permanent records.

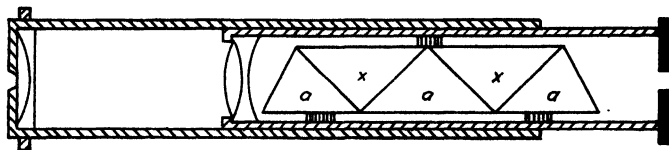


FIG. 34.—The direct-vision spectroscope.

A simpler and less expensive form of instrument is the direct-vision spectroscope (Fig. 34). It is more convenient to use but is less sensitive than the original form.

If the unknown is readily volatile, its spectrum is obtained by introducing the substance into a colorless Bunsen flame by means of a platinum wire; if it is difficultly volatile, the substance is placed in a crater in one of the electrodes of an electric arc or spark. In this way, the high temperature necessary to volatilize the material is reached.

Elements Discovered by Spectrum Analysis.—A very noteworthy achievement of spectrum analysis has been the discovery of new elements. No less than 11 have been discovered by its means, *viz.*:

Element	Date	Discoverers
Cesium.....	1860	Bunsen and Kirchhoff
Rubidium.....	1861	Bunsen and Kirchhoff
Thallium.....	1861	Crookes
Indium.....	1863	Reich and Richter
Gallium.....	1875	Boisbaudran
Helium.....	1895	Ramsay
Neon.....	1898	Ramsay and Travers
Krypton.....	1898	Ramsay and Travers
Xenon.....	1898	Ramsay and Travers
Hafnium.....	1922	Coster and von Hevesy
Ilminium.....	1926	Hopkins, Yntema, and Harris

In addition to those in the foregoing list, a number of elements, while not discovered by means of the spectroscope, give spectra that have been used in their identification, *viz.*:

Element	Date	Discoverers
Scandium	1879	Nilson
Dysprosium	1886	Boisbaudran
Germanium	1886	Winkler
Argon	1894	Rayleigh and Ramsay
Europium	1901	Demarcay

CHAPTER XXVII

SYSTEMATIC ANALYSIS

The elaborate procedure used in general unknowns is called *systematic analysis* and looks to obtaining the maximum information about a substance in the minimum time. It involves the detection not only of the major components, but also of the minor components which may be present intentionally or as impurities.

The general nature of the unknown may limit the number of possible components. For example, an ore or a metallurgical product would not contain NH_4^+ , $\text{C}_2\text{H}_3\text{O}_2^-$, $\text{C}_4\text{H}_4\text{O}_6^{--}$, etc.; and a commercial alloy would not contain an alkali metal, and only in rare cases would it contain an alkaline earth metal; the presence of strong oxidizing agents would exclude strong reducing agents; an acid solution would not contain the anions of the unstable acids; etc. To this end, in industrial analysis it is important to have such information as the source of the material and the uses for which it is intended. To illustrate: If the substance is an insecticide, possible components are Pb^{++} , Ca^{++} , Cu^{++} , AsO_4^{--} , F^- , etc. In the same way, when the material is known to be a baking powder, or a fertilizer, or a pigment, the range of composition is more or less defined.

Preliminary Examination.—An optical examination may be highly informative in the case of a solid unknown. If it is distinctly heterogeneous, it may be crushed and spread out on a piece of glazed paper, and the various physical components sorted by their appearance. Each component is then identified, and the gross composition inferred. In this way, a substance may be known to consist of NaCl and CuSO_4 and not of Na_2SO_4 and CuCl_2 . The actual components of Portland cement have been identified by the optical method.

Formerly it was customary to put an unknown through a number of preliminary tests, such as behavior on ignition (page 421), flame tests (page 422), borax or metaphosphate bead tests (page

420), heating with concentrated H_2SO_4 (page 318), etc. These tests are now considered important only in the detection of organic matter and the identification of simple substances. Again it is urged that the use of flame and bead tests on mixtures leads to error more frequently than to truth.

SOLUTIONS

If the unknown is in the form of a solution, the following points are significant.

Color.—The color should be noted, and ions or molecules proposed to account for it.

Acidity and Alkalinity.—The acidity or alkalinity of the solution has considerable significance. An acid solution can contain none of the anions of the unstable acids (HNO_2 , H_2CO_3 , $\text{H}_2\text{S}_2\text{O}_3$, HClO_3), and probably none of the very volatile acids (H_2S , HCN , etc.) or the readily oxidizable acids (HI , H_2S , H_2SO_3 , etc.). An alkaline solution (provided that organic matter, NH_3 , or complexing anions are absent) can contain, in addition to K^+ and Na^+ , only the cations of those metals which form amphoteric hydroxides (see page 111). A neutral solution, generally speaking, can contain only the ions of salts soluble in water. There are exceptions to this statement, owing to the formation of stable complexes; *e.g.*, PbSO_4 is soluble in the presence of $\text{C}_2\text{H}_3\text{O}_2^-$, MgCO_3 is soluble in the presence of NH_4^+ , etc. Solutions containing free NH_3 can contain, in addition to cation Groups IV and V, the ions Ag^+ , Cu^{++} , Cd^{++} , Zn^{++} , Co^{++} , and Ni^{++} . Alkaline sulfide solutions can contain only the Tin subgroup and Groups IV and V.

Concentration.—It is important to know approximately the amount of dissolved material in a solution, so as to know how large a sample should be taken for an analysis. This information is obtained by evaporating a definite volume of the solution to dryness on a watch glass over a water bath. Occasionally the product is a heavy liquid, which must be allowed to cool in order for it to pass into the solid form. Very deliquescent substances show this behavior, as, for example, FeCl_3 and $\text{Na}_2\text{S}_2\text{O}_3$. The absence of a residue indicates the presence of very volatile materials only, such as NH_3 or HCl , but no members of the usual cation groups.

METALS AND ALLOYS

Metallic unknowns require certain differences in procedure from ordinary unknowns. Not only are the nonmetals absent, but there are limitations to the possible composition of alloys (see the following paragraphs). This makes it possible to take short cuts in many instances. A timely suggestion to the beginner: *Do not take too large a sample for analysis; one-half of a gram is ample.*

Composition of Alloys.—Industrial alloys never contain sodium or potassium, for these metals are too reactive for their alloys to be permanent in the air. Calcium, strontium, and barium are found only rarely. In the next place, the composition of alloys is limited by the miscibility of molten metals. Molten lead and molten iron will not mix; consequently there can be no alloy of these two metals.

If the general nature of an alloy is known, or one or more of its major components, the absence of certain ingredients may be

TABLE 46.—COMPOSITION OF ALLOYS

	Major ingredients	Minor ingredients
Iron alloys.....	Fe	Mn, Ni, Cr, W, Mo, C, Si
Brasses.....	Cu, Zn	Pb, Sn, Fe, Ni, Al, P
Bronzes.....	Cu, Sn	Zn, Pb, Al, Mn, Ni, Fe, As, Si, P
Bearing metals:		
Babbitts.....	Sn, Sb, Cu	
Lead alloys.....	Pb, Sb	Sn, Cu
Bronzes.....	Cu, Sn, Pb	Sb, Bi, Zn, As, etc.
Printers' alloys.....	Pb, Sn, Sb	Cu
Fusible alloys.....	Pb, Bi, Sn	Cd
Light alloys.....	Al, Mg	Cu, Mn
Jewelers' alloys:		
Silver.....	Ag, Cu	Zn, Sn, Ni
Gold.....	Au	Ag, Cu, Cd, Ni, Zn, Pd, Fe, etc.
Tinners' alloys.....	Pb, Sn	Bi, Zn, etc.
Resistance metals.....	Ni, Cr	Fe, Mn, Cu, Zn
Noncorroding alloys:		
German silver.....	Cu, Ni, Zn	
Stellite.....	Cr, Co or Ni	Mo, W, C, etc.
Monel.....	Cu, Ni	Fe, Mn, Si

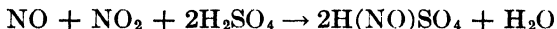
predicted with comparative certainty. For example, the only common metals that are to be expected in an iron alloy are chromium, manganese, nickel, and cobalt. The general composition of the most important classes of alloys is given in Table 46.

Nonmetals in Alloys.—As indicated in Table 46, carbon, phosphorus, and silicon are sometimes found in alloys. After solution of the alloys in an oxidizing solvent, they are left in the following forms: carbon as graphite, sometimes so finely divided as to give the solution a brown color; phosphorus as H_3PO_4 ; silicon as gelatinous silica, $\text{SiO}_2 \cdot x\text{H}_2\text{O}$. The carbon and silica are removed by filtration and identified as follows: The carbon may be proved by dropping a small amount into fused KClO_3 or KNO_3 , producing a flash of flame. The silica is shown by the SiF_4 test for SiO_2 . H_3PO_4 (in the absence of H_3AsO_4) may be detected by the $(\text{NH}_4)_2\text{MoO}_4$ reaction on a portion of the solution.

Dissolving the Material.—The e.m.f. series indicates that only those metals above hydrogen in the series should dissolve in HCl , and the speed of the solution should diminish as hydrogen is approached. Furthermore, HCl is unsuited as a solvent for materials containing silver and lead, for the insoluble AgCl and PbCl_2 form insoluble coatings which interfere with the reaction. Again, the presence of active metals tends to convert arsenic and antimony into the volatile AsH_3 and SbH_3 , which are lost. HNO_3 , on the other hand, dissolves all the common metals except tin and antimony and, under certain conditions, aluminum, chromium, and iron. In such cases, HCl or aqua regia must be used. The best procedure in selecting a solvent is to try dilute HNO_3 first; if it is ineffective, to try HCl ; if neither is sufficient, to try aqua regia, dilute and concentrated.

Removal of Organic Matter.—Organic matter interferes in cation analysis not only by (1) its reducing action, but also, and mainly, by (2) its peptizing action. Illustrative of the latter is the nonprecipitation of AgCl in the presence of gelatin, albumen, etc. Instead of the usual curdy precipitate, only a turbid opalescence appears, which shows little tendency to precipitate out. Another example—certain hydroxides, such as $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$, cannot be precipitated in the presence of tartrates, sugars, and a number of other organic compounds containing two or more hydroxyl groups.

Organic matter is removed by oxidation, most frequently by boiling with HNO_3 in the presence of concentrated H_2SO_4 . The latter aids the reaction, not only by removing water and thereby concentrating the other materials, but by forming with NO and NO_2 nitrosyl sulfuric acid (nitrose), $\text{H}(\text{NO})\text{SO}_4$, which has a higher boiling point than HNO_3 .



This permits digestion at a higher temperature, without loss of HNO_3 . The reaction is continued until SO_3 fumes are evolved. If the solution is not clear (not necessarily colorless), more HNO_3 should be added and the digestion repeated.

Warning.—This digestion with HNO_3 - H_2SO_4 mixture should not be carried out on substances containing glycerin or its derivatives. Glyceryl nitrate (nitroglycerin) would be formed, and a terrific explosion might occur. Certain other compounds besides glycerin—phenol (carbolic acid), for example—form highly explosive compounds. This emphasizes the previous statement (page 428) that it is important to know the general nature of a substance before selecting the analytical procedure.

Organic matter may also be removed by fusion with Na_2CO_3 in the presence of such oxidizing agents as KClO_3 , KNO_3 , and Na_2O_2 . This procedure is apt to cause the loss of volatile materials, particularly mercury and arsenic compounds. Both methods destroy the unstable anions.

Regulation of Acidity.—The sulfides of Group II can be precipitated from solutions containing as high a concentration of H^+ as 0.3 molar, whereas a concentration of 0.25 M H^+ is sufficient to prevent the precipitation of the sulfides of Group III. The free acidity must therefore be reduced to this range in order to effect a clean separation of these groups. This is done by evaporating all the free acid and then adding the theoretical amount. Since HgCl_2 , AsCl_3 , and other chlorides to a less degree, are volatile, chlorides are converted into nitrates or sulfates by adding an excess of HNO_3 or H_2SO_4 before starting the evaporation. Oxalates are imperfectly removed by this procedure.

SOLIDS, NOT METALS OR ALLOYS

By way of a preliminary examination, the color, density, hardness, melting point, appearance upon corrosion by air, etc., should be noted.

Solution of Solids.—Bringing a solid unknown into solution is frequently a difficult procedure. However, if these difficulties are properly interpreted and overcome, very valuable information about the composition of the material may be obtained. The student's impulse to use aqua regia as the solvent in all cases is a natural one, even though it is seldom correct. The proper solvent should be determined by trial on small samples of the finely pulverized unknown. The following solvents should be tried in the order given:

1. Water, cold and hot.
2. Dilute HNO_3 .
3. Dilute HCl .
4. Dilute aqua regia.

If any of these solvents is effective, it should be continued as long as it has any effect. Then another solvent should be tried on the residue. Any residue insoluble in acids should be treated by one of the fusion methods described on pages 434–435. The partial solutions obtained in this way may be kept separate, each constituting a separate unknown. In general, this procedure simplifies the analysis, because these “sub-unknowns” are much easier to analyze than the combined solution.

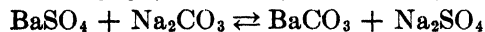
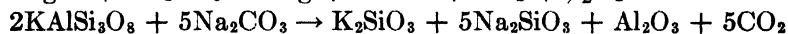
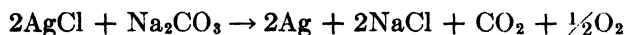
Nitric acid is usually preferable to HCl as a solvent for the following reasons: (1) Nitrates are more generally soluble than chlorides. (2) Nitrates are less volatile than chlorides; so that there is not the danger of losing volatile materials like HgCl_2 , AsCl_3 , etc., during evaporation. (3) HNO_3 , by reason of its oxidizing action, converts many compounds into more stable forms, as, for example, As_2O_3 into H_3AsO_4 .

The practice of adding an excess of acids to the unknown and then boiling it out again before it has a chance to react cannot be condemned too strongly. Of course, heating the solvent helps, but it should not be vigorously boiled. The best procedure is to allow the digestion to proceed on a steam bath, when little of the solvent will be lost. The use of unnecessary volumes of solvents is bad for another reason: it takes time to boil them out, and they vitiate the air in the laboratory.

Students are sometimes surprised to find that dilute acids are better solvents than concentrated acids. The reason is that water is needed to act as a solvent for the products formed in the reaction.

Substances Insoluble in Acids.—The residue insoluble in aqua regia may contain such substances as AgCl, PbCrO₄ (fused), PbSO₄, SnO₂, Al₂O₃, Cr₂O₃, BaSO₄, SrSO₄, CaSO₄, CaF₂, Fe₄[Fe(CN)₄]₃, many silicates, SiO₂, C, and S. The methods to be used in converting these materials into soluble compounds vary with the nature of the materials, so that the proper procedure is to be determined by trial. The most important procedures are as follows.

Transposition with Alkaline Carbonates.—The material is fused with an excess of Na₂CO₃ or K₂CO₃ (see page 419), by which most of the substances are more or less completely transposed; *e.g.*,



Sometimes an oxidizing agent, such as KNO₃, is added to facilitate the reaction with Cr₂O₃ and other oxidizable materials.



After powdering, the melt is extracted, first with hot water, giving a solution that contains the anions of the original, and then with dilute HNO₃ or HCl, giving a solution of the cations. While the decomposition is not complete in all cases, enough of the substance is brought into solution to give satisfactory qualitative tests.

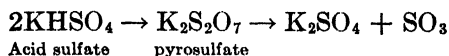
This fusion is best carried out in a platinum crucible. However, should the material contain compounds of any of the easily reducible metals that alloy with platinum (such as Pb, Ag, Bi, or Sn), or strong alkalis, nitrates, FeCl₃, S, As, etc., the platinum would be ruined. The absence of these substances must be known before such a fusion is made. In case of doubt, other methods should be used.

Many substances formed by precipitation but not ignited may be decomposed by boiling with concentrated Na₂CO₃ solution. In principle, the method is identical with the fusion procedure. With compounds of high insolubility, several digestions may be necessary for complete transformation of the materials.

Hydrofluoric Acid Method.—Silicates insoluble in ordinary acids are soluble in hydrofluoric acid, expelling the silicon as

silicon tetrafluoride, SiF_4 . H_2SO_4 is sometimes added as an auxiliary solvent. The reaction must be carried out in platinum vessels, for HF attacks glass and porcelain ware. The operation must be performed in an efficient hood, as both HF and SiF_4 fumes are highly poisonous.

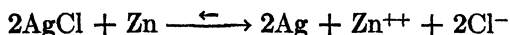
Fusion with KHSO_4 .—Many acid-insoluble compounds are "opened up" by fusion with KHSO_4 . Upon heating, the following decompositions occur:



It will be seen that this procedure amounts to treating the substance with concentrated H_2SO_4 , only at a much higher temperature. Substances not "opened up" by this treatment are PbSO_4 , BaSO_4 , SrSO_4 , SnO_2 , SiO_2 , and certain silicates. The procedure has the advantage that it may be carried out in a porcelain crucible, the expense and hazard of platinum being thereby avoided.

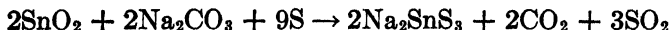
Special Methods.—A number of methods are available for special cases.

Silver Halides.— AgCl , AgBr , etc., are reduced to metallic silver by Zn in the presence of dilute H_2SO_4 ; *e.g.*,



After filtering, the residue is examined for Ag , and the filtrate for the halide ions.

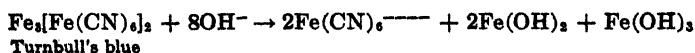
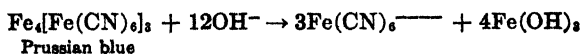
Stannic Oxide.—Native or ignited SnO_2 is converted into soluble sodium thiostannate by fusion with sulfur and sodium carbonate:



When the melt is extracted with hot water, the Na_2SnS_3 dissolves, leaving a residue containing any sulfides of the metals of Groups I and III and the Copper subgroup.

Insoluble Sulfates.— PbSO_4 , BaSO_4 , etc., are reduced by heating with charcoal, giving products soluble in acids (see page 423).

Complex Cyanides.—The complex cyanides of Fe and similar metals are decomposed by strong alkalies; *e.g.*,



Exercises

1. Why is arsenic (except in traces) absent from alloys?
2. In general, what are the probable components of domestic water softeners?
3. How would you test sublimed white lead ($\text{PbSO}_4 + \text{PbO} + \text{ZnO}$) for adulteration with CaSO_4 ?
4. Why will $\text{Pb}(\text{OH})_2$ dissolve better in dilute than in concentrated HNO_3 ?
5. What metals may be presumed to be absent from a lead-tin alloy (e.g., tinner's solder)?
6. Which would be the better way to analyze one of the torpedoes used in Fourth of July celebrations—physical or chemical separation? Just how would you proceed?
7. Explain the result when a flame test is made on a silver salt.
8. How would you determine whether the lead oxide in a solid is Pb_3O_4 or PbO_2 ?
9. A potassium salt dissolves in water giving a neutral solution. Which of the following anions could be present: CO_3^{--} , NO_3^- , SCN^- , $\text{C}_2\text{H}_3\text{O}_2^-$, SO_4^{--} , PO_4^{--} ?
10. A solution of chlorides is neutral to litmus paper. Name five cations that could not be present.
11. Describe the result when it is attempted to dissolve $\text{Fe}_2(\text{SO}_4)_3$ in water.
12. A solution, smelling strongly of NH_3 , is boiled until odorless. It is still strongly alkaline. What cations could be present in quantity? In traces? What metals could be present as anions?
13. A solution contains considerable $\text{Na}_2\text{S}_2\text{O}_3$. What cations could be present?
14. A strongly acid solution contains MnO_4^- . What anions could be present?
15. A student, upon attempting to dissolve an alloy in hot dilute HNO_3 , noted that it melted below the boiling point of water. What inference should he have drawn?
16. Name some metals never present in ferrous alloys except in traces.
17. In what forms are C, P, and Si probably present in ferrous alloys?
18. An inexperienced analyst found no Al in a baking powder that actually contained alum. Suggest his error.
19. In the HNO_3 digestion to remove organic matter from an unknown, what form of apparatus should be used?
20. How would you proceed to test the coatings of photographic dry plate for AgBr?
21. A food stuff—bread, for example—is suspected of containing As_2O_3 . How would you carry out the test? (Do not use a micro test.)
22. Why is the ready oxidation of $\text{H}_2\text{C}_2\text{O}_4$ by HNO_3 not to be expected?
23. What volume of concentrated H_2SO_4 (18 molar) should be present in 100 cc. of solution to give 0.25 M H^+ ? Regard the H_2SO_4 as completely ionized.

24. Name two metals soluble in HCl, but insoluble in HNO₃.

25. How would you bring into solution an unknown containing fused PbCrO₄, PbO₂, and MnO₂?

26. Refer to the Solubility Table, and suggest a set of reagents other than hot water and NH₃ solution that might be used in separating PbCl₂, AgCl, and Hg₂Cl₂.

27. Explain why each of the following unknown reports could not be correct:

(a) An acid solution reported to contain MnO₄⁻, AsO₃⁻⁻⁻, PO₄⁻⁻⁻.

(b) A water-soluble unknown reported to contain Ba⁺⁺, Cu⁺⁺, Na⁺, Fe(CN)₆⁻⁻⁻, Cl⁻, SO₄⁻⁻⁻.

(c) An acidic solution reported to contain Na⁺, K⁺, Fe⁺⁺, NO₂⁻, Cl⁻, SO₄⁻⁻⁻.

(d) An acidic solution reported to contain Cl⁻, CO₃⁻⁻⁻, I⁻, Cr₂O₇⁻⁻⁻.

28. Suppose that Ba⁺⁺ were "carried down" in the precipitation of Group II sulfides. Where, and in what form, would it appear in the Group II analysis?

29. Suppose Cu₂⁺⁺ ions were stable enough to exist in contact with the air. To what cation group would Cu₂⁺⁺ belong? Modify the procedure for this group so as to include this ion.

30. Cite three places where NH₄⁺ interferes in cation analysis, and one place in anion analysis. What is the nature of each interference, and how can each be avoided?

31. By means of a system of braces and arrows, trace the products formed when SnS is treated by the following reagents, one following the other: (a) heat and (NH₄)₂S_x, (b) dilute HCl, (c) heating with concentrated HClO₄, (d) H₂S + H₂C₂O₄, (e) boiling with Pb, (f) HgCl₂.

32. A white sodium salt is soluble in water, forming a colorless solution. AgNO₃ is added, at first giving no precipitate but then, with excess AgNO₃, a white precipitate. Upon boiling, the precipitate turns black, and the mother solution becomes distinctly acid. Identify the salt.

33. Give two reasons why Zn(ClO₄)₂ rather than HClO₄ is used to precipitate K⁺.

34. The Iron subgroup precipitate in Group III is white. Assuming correct technique, list the formulas of eight white compounds that might be present.

35. Why does H₂S give no precipitate with Zn⁺⁺ in dilute HCl solution? Why should the addition of excess NaC₂H₃O₂ cause ZnS to form?

36. FeSO₄ reduces Hg(NO₃)₂ solution to free mercury, but not HgCl₂. Explain.

37. A solution of Na⁺ and K⁺ salts gives with Ag⁺ a white precipitate, partially soluble in dilute HNO₃, but with Ba⁺⁺ a white precipitate, partially soluble in HNO₃. What anion groups may be present?

38. A red substance dissolves in hot concentrated HCl, forming a colorless solution. Upon dilution with boiled water, a white precipitate is thrown down, turning green when exposed to the air. Suggest an oxide that would fit this description.

39. Suppose that Ag^+ and Hg_2^{++} were carried into Group II by incomplete precipitation in Group I. Where would they appear in the Group II procedure, and what errors (if any) might result?

40. The feldspars are "opened up" by fusion with an alkaline carbonate. How would you test for K and Na?

41. What is ultramarine? How would you distinguish it from Prussian blue?

42. A white powder dissolved in dilute HNO_3 with the evolution of a colorless, odorless, noninflammable gas. This HNO_3 solution gave a white precipitate with AgNO_3 , and the filtrate from this reaction gave a brown precipitate upon careful neutralization with NH_4OH . An HCl solution of the powder gave no reaction with FeCl_3 .

After adjusting the acidity on the HNO_3 solution, H_2S in the presence of NH_4I gave a yellow precipitate soluble in $(\text{NH}_4)_2\text{S}_2$, but insoluble in concentrated HCl .

The filtrate from the H_2S precipitate was boiled and treated with excess NH_4OH , giving a white precipitate not affected by H_2S , but soluble in NaOH . The filtrate from the NH_4OH precipitation gave a white precipitate with $(\text{NH}_4)_2\text{CO}_3$. This precipitate was dissolved in $\text{HC}_2\text{H}_3\text{O}_2$, and the solution gave no precipitate with $\text{K}_2\text{Cr}_2\text{O}_7 + \text{NaC}_2\text{H}_3\text{O}_2$ but a white precipitate with $\text{K}_4\text{Fe}(\text{CN})_6 + \text{NH}_4\text{Cl}$. The filtrate from the $(\text{NH}_4)_2\text{CO}_3$ precipitation was evaporated with HNO_3 and ignited. The residue was taken up in water, and the solution gave no reaction with $\text{Na}_2\text{HPO}_4 + \text{NH}_4\text{OH}$, none with $\text{Na}_2\text{Co}(\text{NO}_2)_6$, but a yellowish precipitate with the $\text{HZn}(\text{UO}_3)_2(\text{C}_2\text{H}_3\text{O}_2)_2$ reagent.

What ions (not elements) are indicated?

43. A purplish solution (1), containing no Cation Groups I and II, was acidified with HCl and saturated with H_2S , giving a white precipitate (2) in a green solution. After filtering, the solution was made alkaline with NH_4OH and again saturated with H_2S , giving a dark precipitate (A) and a brownish filtrate (3). The dark precipitate (A) was partially soluble in HCl , leaving a black residue, but completely soluble in dilute aqua regia, giving a greenish solution. $\text{NaOH} + \text{Na}_2\text{O}_2$ were added to the green solution, forming a dark brown precipitate (B) and a colorless filtrate (C).

The colorless filtrate (C) was acidified and then made alkaline with NH_4OH without effect. Upon saturation of the ammoniacal solution with H_2S , a white precipitate (4) formed, insoluble in $\text{HC}_2\text{H}_3\text{O}_2$, but soluble in HCl .

The brown precipitate (B) was dissolved in concentrated HNO_3 + a few drops of NaNO_2 solution, and the solution was boiled with KClO_3 , forming a brown precipitate (5). The filtrate from the brown precipitate gave a deep blue color with excess NH_4OH .

The brownish filtrate (3) was acidified with $\text{HC}_2\text{H}_3\text{O}_2$ and concentrated to 25 cc. The gray precipitate (6) that formed was discarded. The clear filtrate was treated with $\text{NH}_4\text{OH} + (\text{NH}_4)_2\text{CO}_3$, forming a white precipitate (D) in a colorless filtrate (E). Precipitate (D) was dissolved in $\text{HC}_2\text{H}_3\text{O}_2$, and the solution gave the following reactions: No precipitate with $\text{K}_2\text{Cr}_2\text{O}_7 +$

$\text{NaC}_2\text{H}_3\text{O}_2$, no precipitate with $\text{NH}_4\text{Cl} + \text{K}_4\text{Fe}(\text{CN})_6$, but a white precipitate (7) with H_2SO_4 .

Filtrate (E) was evaporated and ignited to expel NH_4^+ salts. The residue was dissolved in water; and the solution gave no reaction with $\text{Na}_2\text{HPO}_4 + \text{NH}_4\text{OH}$, none with $\text{Na}_3\text{Co}(\text{NO}_2)_6$, but a white precipitate (8) with alcoholic H_2SiF_6 .

Name the substances (molecules or ions) responsible for the numbered (not the lettered) reactions.

44. What compounds are indicated in the following mixture?

A grayish mixture was extracted successively with (1) ether, (2) H_2O , (3) $\text{HC}_2\text{H}_3\text{O}_2$, and (4) dilute HCl , leaving (5) a creamy residue.

1. The ether extract was blue. The solvent was evaporated and the residue taken up in water, giving a pink solution. NH_4OH was added, giving a straw-colored solution, and next H_2S , giving a black precipitate practically insoluble in dilute HCl . The filtrate from this black precipitate gave with Ag^+ , a white precipitate soluble in NH_4OH and with Fe^{+++} a deep red color.

2. The residue insoluble in ether was extracted with water, and the aqueous extract divided into two portions. The first portion was treated successively with HCl , H_2S , $\text{NH}_4\text{OH} + \text{H}_2\text{S}$, and $(\text{NH}_4)_2\text{CO}_3$ without effect. With H_2SiF_6 it gave a white precipitate, insoluble in alcohol, but no reaction with $\text{Na}_3\text{Co}(\text{NO}_2)_6$. The second portion gave a yellow precipitate upon warming with $(\text{NH}_4)_2\text{MoO}_4 + \text{HNO}_3$.

3. The residue from the water extraction was treated with $\text{HC}_2\text{H}_3\text{O}_2$, and a colorless gas was evolved that gave a white precipitate with $\text{Ca}(\text{OH})_2$ but did not bleach acidified KMnO_4 . The residue insoluble in $\text{HC}_2\text{H}_3\text{O}_2$ was filtered out and reserved for (4). The filtrate from this residue gave with H_2S a white precipitate soluble in dilute HCl .

4. The dark residue from (3) was boiled with HCl , liberating a yellowish gas which bleached litmus. The undissolved residue having been reserved for (5), the filtrate was treated with NaOH , giving a white-to-tan precipitate, which darkened rapidly in contact with air.

5. The residue from (4) was found to be slightly soluble in NH_4OH . Upon adding H_2SO_4 and metallic Zn , this residue was slowly transposed, leaving a black solid and a colorless solution. The solid was dissolved in HNO_3 , and HCl added, giving a white precipitate, readily soluble in NH_4OH . The solution was treated with Cl_2 , forming a yellow solution. Upon shaking with CCl_4 , the latter extracted the color as a reddish layer.

45. An alloy dissolved slowly in aqua regia, giving a green solution. After regulation of the acidity, the solution was saturated with H_2S , forming a small white precipitate (1). Precipitate (1) was filtered out and dissolved in $(\text{NH}_4)_2\text{S}$. Upon acidification of this solution with HCl , a second white precipitate formed, insoluble in concentrated HCl , but soluble in concentrated HClO_4 (hot). This solution was diluted and saturated with H_2S without effect.

The filtrate from precipitate (1) was boiled to expel H_2S , and a slight excess of NH_4OH was added, forming a dirty green precipitate in a blue

solution. Upon saturating with H_2S , the product was a black precipitate in a colorless solution. After filtering, the precipitate was found to be partially soluble in dilute HCl and completely soluble in dilute aqua regia. Boiling this solution with NaOH and Na_2O_2 produced a brownish-green precipitate (2) in a deep-yellow solution (3).

Solution (3) was acidified with HCl and then made alkaline with NH_4OH with no effect except slight color changes. Excess $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ was added, the precipitate removed by filtration, and the filtrate saturated with H_2S without effect.

Precipitate (2) was dissolved in concentrated HNO_3 , and KClO_3 was added to the boiling solution, giving a slight brown precipitate. The filtrate from this precipitation gave a slight reddish brown precipitate in a deep-blue solution upon treatment with excess NH_4OH .

The original solution gave with AgNO_3 a heavy white precipitate soluble in excess NH_4OH and a brownish coloration when mixed with FeSO_4 and placed in contact with concentrated H_2SO_4 .

List in two separate lists (a) the major and (b) the minor constituents of the unknown.

TABLE OF SOLUBILITIES

	Acetate	Arsenate	Arsenite	Borate	Bromide	Carbonate	Chlorate	Chloride
Aluminum	Water	Acids	(3)	Acids	Water	Water	Water
Ammonium	Water	Water	Water	Water	Water	Water	Water	Water
Antimony	HBr	HCl
Arsenic	HBr	HCl
Barium	Water	Acids	Acids	Acids	Water	Acids	Water	Water
				(2)				
Bismuth	Water	Acids	Acids	HBr	Acids	Water	HCl
Cadmium	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Calcium	Water	Acids	Acids	(1)	Water	Acids	Water	Water
Chromium (ic)	Water	Acids	(3)	Acids	Water	Water	Water
								or Insol.
Cobalt	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Copper (cupric)	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Ferric	Cold	Acids	Acids	Acids	Water	Water	Water
	Water							
Ferrous	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Lead	Water	HNO ₃	HNO ₃	HNO ₃	(1)	HNO ₃	Water	Hot
								water
Magnesium	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Manganese	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Mercuric	Water	Acids	Acids	Water	Acids	Water	Water
Mercurous	(1)	Acids	Acids	HNO ₃	HNO ₃	Water	HNO ₃
					Br ₂			Cl ₂
Nickel	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Potassium	Water	Water	Water	Water	Water	Water	Water	Water
Silver	(1)	HNO ₃	HNO ₃	HNO ₃	KCN	HNO ₃	Water	NH ₄ OH
								KCN
Sodium	Water	Water	Water	Water	Water	Water	Water	Water
Stannic	Water	Acids	Water	Water
Stannous	Water	Acids	Acids	Acids	Water	Water
Strontium	Water	Acids	Acids	(1)	Water	Acids	Water
Zinc	Water	Acids	Acids	Acids	Water	Acids	Water	Water

Key to Abbreviations and References.—"Alks." = NaOH, KOH; "Insol." = insoluble in acids; (1) = slightly soluble in water; (2) = soluble in solutions of ammonium salts; (3) = hydrolyzed by water; (4) = soluble in ammonium acetate solution; (5) = acid of anion decomposed with precipitate formation.

(6) Many insoluble cyanides, oxalates, tartrates, and thiosulfates are soluble in solutions of salts containing the anion involved. (7) Native silicates are generally insoluble in acids; decomposition by acids is limited almost wholly to precipitated silicates.

TABLE OF SOLUBILITIES (Continued)

	Chromate	Cyanide (6)	Ferricyanide	Ferrocyanide	Fluoride	Fluosilicate	Hydroxide
Aluminum	Acids	(3)	Acids	Water	Water	Acids Alks.
Ammonium.....	Water	Water	Water	Water	Water	Water (3)	Water
Antimony.....	(1)	Acids Alks.
Arsenic.....	Acids Alks.
Barium.....	Acids	(1)	Water	Water	HNO ₃	Acids	(1)
Bismuth.....	Acids	(3)	Acids	Acids	Water	Acids
Cadmium.....	Acids	(1)	(1)	Water	Acids
Calcium.....	Water	Water	Water	(1)	Insol.	(1)	NH ₄ OH
Chromium (ic).....	Acids	Water	Water	(1)
Cobalt.....	Acids	Acids	Insol.	Insol.	(1)	Water	Acids
Copper (cupric).....	Water	Insol.	Insol.	(1)	Water	NH ₄ OH Acids
Ferrio.....	Water	Water	Insol.	(1)	Water	NH ₄ OH Acids
Ferrous.....	Insol.	Insol.	(1)	Water	Acids
Lead.....	HNO ₃	(1)	(1)	Insol.	(1)	Water	HNO ₃ Alks.
Magnesium.....	Water	Water	Water	Water	Acids	Water	Acids (2)
Manganese.....	Acids	Insol.	Acids	Acids	Water	Acids
Mercuric.....	Acids	Water	Acids	Water	Water	
Mercurous.....	Acids	Acids	Water	(1)	
Nickel.....	Acids	Hot acids	Insol.	Insol.	(1)	Water	Acids
Potassium.....	Water	Water	Water	Water	Water	(1)	NH ₄ OH Water
Silver.....	HNO ₃	Conc. HNO ₃	Insol.	Insol.	Water	Water	
Sodium.....	Water	Water	Water	Water	Water	(1)	Water
Stannic.....	Acid	Insol.	Water	Acids Alks.
Stannous.....	Insol.	Water	Acids Alks.
Strontium.....	(1)	Water	Water	Water	Acids	Water	(1)
Zinc.....	Acids	Acids	Acids	Insol.	Acids	Water	Acids Alks. NH ₄ OH

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TABLE OF SOLUBILITIES (*Continued*)

	Iodide	Nitrate	Nitrite	Oxalate (6)	Oxide	Perchlorate	Permanganate	Phosphate
Aluminum	Water	Water	(3)	Acids	Acids or Insol.	Water	Water	Acids
Ammonium	Water	Water	Water	Water	Water	Water	Water
Antimony	(3)	(3)	Acids Alks.			
Arsenic	Water	Acids Alks.			
Barium	Water	Water	Water	Acids	(1)	Water	Water	Acids
Bismuth	Acids	HNO ₃	(3)	Acids	Acids	Acids
Cadmium	Water	Water	Water	Acids	Acids	Water	Water	Acids
Calcium	Water	Water	Water	Strong acids	(1)	Water	Water	Acids
Chromium (ic)	Water	Water	(3)	(1)	Acids or Insol.	Water	Water	Acids
Cobalt	Water	Water	Water	Acids	Acids	Water	Water	Acids
Copper (cupric)	Water	Water	Acids	Acids	Water	Water	Acids
Ferrie	Water	Water	Acids	Acids	Water	Water	Acids
Ferrous	Water	Water	Water	Acids	Acids	Acids
Lead	(1)	Water	Water	HNO ₃	Acids	Water	Water	HNO ₃
Magnesium	Water	Water	Water	Water	Acids	Water	Water	Acids
Manganese	Water	Water	Water	Acids	Acids	Water	Water	Acids
Mercuric	Acids	Water	Water	Acids	Acids	Water	Water	Acids
Mercurous	HNO ₃	HNO ₃	(3)	HNO ₃	HNO ₃	Water	HNO ₃
Nickel	Water	Water	Water	Acids	Acids	Water	Water	Acids
Potassium	Water	Water	Water	Water	(1)	Water	Water
Silver	KCN	Water	(1)	HNO ₃	HNO ₃	Water	Water	HNO ₃
Sodium	Water	Water	Water	Water	Water	Water	Water
Stannic	(3)	(3)	Water	Acids Alks. Insol.	Water	Water	Acids
Stannous	Water	Acids	Acids Alks.	Water	Acids
Strontium	Water	Water	Water	Acids	(1)	Water	Water	Acids
Zinc	Water	Water	Water	Acids	Acids	Water	Water	Acids

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TABLE OF SOLUBILITIES (Continued)

	Silicate (7)	Sulfate	Sulfide	Sulfite	Tartrate (6)	Thiocyanate	Thiosulphate (6)
Aluminum	Acids (5)	Water	(3)	Acids	Water	Water	Water
Ammonium	(3)	Water	Water	Water	Water	Water	Water
Antimony	Conc. acids	Acids
Arsenic	HNO ₃ or Aqua Regia
Barium	Acids (5)	Insol.	(3)	Acids	Acids	Water	(1)
Bismuth	Acids (5)	H ₂ SO ₄	HNO ₃	Acids
Cadmium	Acids (5)	Water	Acids	Acids	(1)	(1)	Water
Calcium	Acids (5)	(1)	(3)	Acids	Acids	Water	Water
Chromium (ic)	Acids (5)	Water	(3)	Water	Water
Cobalt	Acids (5)	Water	HNO ₃	Acids	Water	Water	Water
Copper (cupric)	Acids (5)	Water	HNO ₃	Acids	Water
Ferri	Acids (5)	Water	Acids	Water	Water
Ferrous	Acids (5)	Water	Acids	Acids	(1)	Water	Water
Lead	HNO ₃ (5)	(4)	HNO ₃	HNO ₃	HNO ₃	(1)	HNO ₃ (5)
Magnesium	Acids (5)	Water	(3)	Water	Water	Water	Water
Manganese	Acids (5)	Water	(2)	Acids	(1)	Water	Water
Mercuric	H ₂ SO ₄	Aqua Regia	Acids	Acids	(1)
Mercurous	(1)	Aqua Regia	(1)	Acids
Nickel	Acids (5)	Water	HNO ₃	Acids	Acids	Water	Water
Potassium	Water	Water	Water	Water	Water	Water	Water
Silver	HNO ₃ (5)	Water	Conc. HNO ₃	HNO ₃	HNO ₃	HNO ₃ (5)	HNO ₃ (5)
Sodium	Water	Water	Water	Water	Water	Water	Water
Stannic	H ₂ SO ₄	Acids	Water	Water	Water
Stannous	H ₂ SO ₄	Acids	Acids	Acids	Water	Water
Strontium	Acids (5)	Insol.	(3)	Acids	Acids	Water	Water
Zinc	Acids (5)	Water	(2)	Acids	Acids	Water	Water

Key to Abbreviations and References.—"Alks." = NaOH, KOH; "Insol." = insoluble in acids; (1) = slightly soluble in water; (2) = soluble in solutions of ammonium salts; (3) = hydrolyzed by water; (4) = soluble in ammonium acetate solution; (5) = acid of anion decomposed with precipitate formation.

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